

## 6.0 EMISSIONS FROM COMBUSTION SOURCES

Mercury is often found as a trace contaminant in fossil fuels or waste materials. When these materials are combusted, the combination of the elevated temperature of the process and the volatility of mercury and mercury compounds results in mercury being emitted in the combustion gas exhaust stream. This section addresses mercury and mercury compound emissions from seven stationary source combustion processes:

- Coal combustion
- Oil combustion
- Wood combustion
- Municipal waste combustion
- Sewage sludge incineration
- Hazardous waste combustion
- Medical waste incineration

These seven processes fall into two general categories. The first three involve fuel combustion for energy, steam, and heat generation, while the last four are primarily waste disposal processes, although some energy may be recovered from these processes. A summary of the estimated emissions from each of the above categories is as follows:

Category	Emissions, Mg (tons)
Coal combustion	67.8 (74.6)
Oil combustion	7.4 (8.1)
Wood combustion	0.1 (0.1)
Municipal waste combustion	26 (29)
Sewage sludge incineration	0.86 (0.94)
Hazardous waste combustion	6.3 (6.9)
Medical waste incineration	14.5 (16)

The paragraphs below provide a general introduction to the two combustion categories. As part of this introduction, a summary of nationwide fuel usage is presented in detail. This information was used to develop nationwide emissions of mercury for different sectors and fuels.

In 1994, the total annual nationwide energy consumption in the United States was  $93.584 \times 10^{12}$  megajoules (MJ) ( $88.789 \times 10^{15}$  British thermal units [Btu]).<sup>39</sup> Of this total, about  $54.889 \times 10^{12}$  MJ ( $52.077 \times 10^{15}$  Btu) or 59 percent involved consumption of coal, petroleum products, and natural gas in nontransportation combustion processes. (No data were available on energy consumption for wood combustion from the U.S. Department of Energy.) Table 6-1 summarizes the 1994 U.S. distribution of fossil fuel combustion as a function of fuel type in the utility, industrial, commercial, and residential sectors. The paragraphs below provide brief summaries of fuel use patterns; additional details on fuel consumption by sector for each State can be found in "State Energy Data Report, Consumption Estimates, 1994"<sup>39</sup>.

As shown in Table 6-1, at  $22.129 \times 10^{12}$  MJ ( $20.995 \times 10^{15}$  Btu) per year, the industrial sector is the largest consumer of fossil fuels. This sector uses a mixture of natural gas (46 percent), fuel oil (7 percent), other petroleum fuels (35 percent), and coal (12 percent). The other petroleum fuels that are

TABLE 6-1. 1994 DISTRIBUTION OF FOSSIL FUEL CONSUMPTION IN THE UNITED STATES

Fuel	Annual energy consumption, 10 <sup>12</sup> MJ (10 <sup>15</sup> Btu)				
	Utilities	Industrial	Commercial	Residential	Total
Bituminous/lignite coal	17.760 (16.850)	2.642 (2.507)	0.076 (0.072)	0.041 (0.039)	20.519 (19.468)
Anthracite coal	0.018 (0.017)	-- (--)	0.012 (0.011)	0.017 (0.016)	0.047 (0.044)
Distillate oil	0.100 (0.095)	1.169 (1.109)	0.489 (0.464)	0.928 (0.880)	2.686 (2.548)
Residual oil	0.893 (0.847)	0.448 (0.425)	0.184 (0.175)	-- (--)	1.525 (1.447)
Other petroleum fuels	0.027 (0.026)	7.710 (7.315)	0.121 (0.115)	0.485 (0.460)	8.343 (7.916)
Natural gas	3.222 (3.057)	10.160 (9.639)	3.139 (2.978)	5.249 (4.980)	21.770 (20.654)
Total	22.020 (20.892)	22.129 (20.995)	4.021 (3.815)	6.719 (6.375)	54.889 (52.077)

Source: Reference 39.

used include primarily liquified petroleum gas, asphalt and road oil, and other nonclassified fuels. Again, the distribution among the three fuel types varies substantially from State to State, with each of the three contributing significant fractions in most States. Notable exceptions are Hawaii, which relies almost exclusively on petroleum fuels; Alaska, which relies primarily on natural gas; and the northeastern States of Connecticut, New Hampshire, Rhode Island, and Vermont, which use almost no coal.

The utility sector is the second largest fossil fuel energy consumer at the rate of  $22.020 \times 10^{12}$  MJ ( $20.892 \times 10^{15}$  Btu) per year. About 81 percent of this energy was generated from coal combustion, with bituminous and lignite coal contributing substantially greater quantities than anthracite coal. In fact, Pennsylvania is the only State in which anthracite coal is used for electric power generation. Although most States rely primarily on coal for power generation, the distribution among fossil fuels varies from State to State, and several States rely heavily on natural gas and fuel oil for power generation. In California, natural gas provides about 97 percent of the fossil-fuel based electricity production, and no coal is used. In Hawaii, fuel oil is used exclusively, while in Oklahoma and Texas, a mixture of coal and natural gas are used. In Florida, Louisiana, Massachusetts, and New York, coal, fuel oil, and natural gas each represent a substantial fraction of the power generation. The States of Idaho, Maine, Rhode Island, and Vermont have no coal fired utilities. Idaho relies exclusively on hydroelectric power, while the New England States use a mixture of fuel oil, natural gas, nuclear, and hydroelectric power.

As shown in Table 6-1, substantially smaller quantities of fossil fuel are used in the commercial and residential sectors than are used in the utility and industrial sectors. The fuels used are primarily natural gas, fuel oil, and liquified petroleum gas (the "other petroleum fuels" in the residential category). Almost all States use a mixture of the fuels, but the distributions vary substantially, with some States like California and Louisiana using primarily natural gas and others like New Hampshire and Vermont using a much greater fraction of fuel oil. One unique case is Pennsylvania where anthracite coal is used in both the residential and commercial sectors.

In the individual sections below, additional information will be presented on the mercury content of the different fuels and on the relationship between fuel type and emissions. However, for any geographic area, the contribution of energy generation sources to mercury emissions will be a function of the distribution of fuels used in the different sectors within the area.

The sources within the second combustion category are engaged primarily in waste disposal. Mercury emissions from these processes are related to the mercury levels in the waste. The different waste types are generally characterized with distinct source categories.

Furthermore, these waste disposal practices are not strongly related. Consequently, each of these categories will be characterized individually within the sections below rather than in a general discussion here.

The seven sections below have a consistent organization. First, the characteristics of the fuel or waste are described and, in the case of the waste combustion processes, the general source category is also described. Second, process descriptions are presented and emission points are identified. Third, available emission control measures are identified and described. Finally, emission factors are presented. A discussion of the sampling and analytical methods used to determine the mercury emission levels from combustion sources is presented in Section 9.

## 6.1 COAL COMBUSTION

As presented in Table 6-1, most coal combustion in the United States occurs in the utility and industrial sectors, with about 87 percent being bituminous and lignite combustion within the utility sector and about 13 percent being bituminous and lignite combustion in the industrial sector. Consequently, the focus of the discussion below will be on bituminous and lignite coal combustion in utility and industrial boilers. However, limited information on anthracite coal combustion will also be presented.

### 6.1.1 Coal Characteristics

The coal characteristics of greatest interest in evaluating mercury emissions from coal combustion are coal heating values and coal mercury content. Mercury emissions are a direct function of the mercury content, while heating values are used to convert emission factors between mass input-based and heat input-based activity levels. This section briefly summarizes the information about coal heating levels and mercury content.<sup>40,41,42</sup> More complete summaries can be found in Reference 40 and detailed analyses of coal mercury content as a function of coal type and geographic region can be found in Reference 41 and Reference 42.

Coal is a complex combination of organic matter and inorganic ash formed in geologic formations from successive layers of fallen vegetation and other organic matter. Coal types are broadly classified as anthracite, bituminous, subbituminous, or lignite, and classification is made by heating values and amounts of fixed carbon, volatile matter, ash, sulfur, and moisture.<sup>43</sup> Formulas for differentiating coals based on these properties are available.<sup>44</sup> These four coal types are further subdivided into 13 component groups. Table 6-2 summarizes information about the heating values for these component groups.

The heating value of coal varies among coal regions, among mines within a region, among seams within a mine, and within a seam. The variability is minimal compared to that found with trace metal levels described below, but it may be important when fuel heat content is used as the activity level measure for source emission calculations. Data presented in Table 6-3 illustrate the regional variability of coal heat content. Heat content among coals from several different mines within a region appears to exhibit greater variability than either variability within a mine or within a seam. For the sample points presented in Table 6-3, intermine variability averaged 15 percent, intramine variability 7 percent, and intraseam variability 3 percent. Because few combustion sources burn coal from just one seam or one mine, coal heat content variability may significantly affect emission estimates that are being calculated using emission factors, coal use data, and coal heat content data, even if the source gets all its coal from the same area of the country.<sup>40</sup>

To an even greater extent than the heating value, the mercury content of coal varies substantially among coal types, at different locations in the same mine, and across geographic regions. The most comprehensive source of information on coal composition is the United States Geological Survey (USGS) National Coal Resources Data System (NCRDS). Geochemical and trace element data are stored within the USCHEM file of NCRDS. As of October 1982, the file contained information on 7,533 coal samples representing all U.S. coal provinces. Trace element analysis for about 4,400 coal samples were included in the data base. This computerized data system was not accessed during the current study due to time and budgetary constraints and information from USGS that indicated that few data had been added to the system since 1972; however, a summary of the data presented in Reference 40 was reviewed. The most extensive source of published trace element data was produced in Reference 42. This report contains data for 799 coal samples taken from 150 producing mines and includes the most important U.S. coal seams. Data from Reference 42 was the initial input into the USCHEM file of NCRDS. The information presented here summarizes the review presented in Reference 40 of the results published in References 41 and 42. Note that those results are consistent with unpublished analyses conducted by USGS on the data

TABLE 6-2. COAL HEATING VALUES

Coal class	Component group	Definition	Source <sup>a</sup>	Heating value, kJ/kg (Btu/lb)	
				Range <sup>a</sup>	Mean <sup>a</sup>
Anthracite	A1	Meta-anthracite	PA,RI	21,580-29,530 (9,310-12,740)	25,560 (11,030)
	A2	Anthracite	CO,PA,NM	27,700-31,800 (11,950-13,720)	30,270 (13,000)
	A3	Semianthracite	AR,PA,VA	27,460-31,750 (11,850-13,700)	29,800 (12,860)
Bituminous	B1	Low volatile bituminous	AR,MD,OK,PA,WV	30,640-34,140 (13,220-14,730)	32,400 (13,980)
	B2	Medium volatile bituminous	AL,PA,VA	31,360-33,170 (13,530-14,310)	32,170 (13,880)
	B3	High volatile A bituminous	AL,CO,KS,KY,MO,NM,PA,TN,TX,UT,VA,WV	28,340-35,710 (12,230-14,510)	31,170 (13,450)
	B4	High volatile B bituminous	IL,KY,MO,OH,UT,WY	26,190-30,480 (11,300-13,150)	28,480 (12,290)
	B5	High volatile C bituminous	IL,IN,IA,MI	24,450-27,490 (10,550-11,860)	26,030 (11,230)
Subbituminous	S1	Subbituminous A	MT,WA	23,940-25,820 (10,330-11,140)	24,890 (10,740)
	S2	Subbituminous B	WY	21,650-22,270 (9,340-9,610)	21,970 (9,480)
	S3	Subbituminous C	CO,WY	19,280-19,890 (8,320-8,580)	19,580 (8,450)
Lignite	L1	Lignite A	ND,TX	16,130-17,030 (6,960-7,350)	16,660 (7,190)
	L2	Lignite B	NA	NA	NA

Source: Reference 40.

<sup>a</sup>NA = not available.

TABLE 6-3. EXAMPLES OF COAL HEAT CONTENT VARIABILITY

Variability	Coal source	Coal heat content, Btu/lb		Percent variation about the mean
		Mean	Range <sup>a</sup>	
Intermine variability	Eastern U.S.	12,320	10,750 - 13,891	12.7
	Central U.S.	10,772	9,147 - 12,397	15
	Western U.S.	11,227	9,317 - 13,134	17
Intramine variability	Eastern U.S.	12,950	NA	4.8 <sup>b</sup>
		10,008	9,182 - 10,834	8.0
		12,000	11,335 - 12,665	5.5
	Central U.S.	12,480	NA	5.7 <sup>c</sup>
		10,975	9,667 - 12,284	12.0
	Western U.S.	10,351	9,791 - 10,911	5.4
Intraseam variability	Eastern U.S.	12,230	NA	3.0 <sup>d</sup>
	Central U.S.	10,709	10,304 - 11,113	3.7
	Western U.S.	11,540	NA	2.5 <sup>e</sup>

Source: Reference 40.

<sup>a</sup>NA = not available.

<sup>b</sup>Based on a standard deviation of 624.

<sup>c</sup>Based on a standard deviation of 708.

<sup>d</sup>Based on a standard deviation of 371.

<sup>e</sup>Based on a standard deviation of 291.

contained in NCRDS as of 1989.<sup>45</sup> More information on the sampling and analysis of mercury in coal is presented in Section 9.

Table 6-4 presents information on the mean concentration of mercury in coal and on the distributions of mercury concentrations by coal type. Bituminous and anthracite coals have the highest mean mercury concentrations, 0.21 parts per million by weight (ppmwt) and 0.23 ppmwt, respectively. The standard deviation of each mean either approaches or exceeds the mean, indicating strong variation in the data. According to Reference 40 subbituminous coals have the greatest reported range of mercury concentrations (0.01 to 8.0 ppm). Based on conversations with USGS personnel, the means reported in Table 6-4 are regarded as typical values for in-ground mercury concentration in coals in the United States.<sup>45</sup>

TABLE 6-4. MERCURY CONCENTRATION IN COAL BY COAL TYPE

Coal type	No. of samples	Mercury concentration, ppmwt		
		Range	Arithmetic mean	Standard deviation
Bituminous	3,527	<0.01 to 3.3	0.21	0.42
Subbituminous	640	0.01 to 8.0	0.10	0.11
Anthracite	52	0.16 to 0.30	0.23	0.27
Lignite	183	0.03 to 1.0	0.15	0.14

Source: Reference 40.

Other estimates of mercury concentration in coal have been developed. The U. S. EPA, in the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units, used a USGS data base containing analyses of 3,331 core and channel samples of coal from the top 50 (1990 and later) economically feasible coal streams in the U.S.<sup>33,46</sup> Industry reviewed the USGS data set and, under a separate effort, screened the data to remove about 600 entries representing coal seams that could not be mined economically.<sup>47</sup> Because the average mercury concentration of the screened data set was virtually the same as the mercury concentration when the full USGS data set was used, EPA elected to use the USGS data set in its entirety.<sup>33</sup> Other data sets showing concentrations about 50 percent lower than the USGS data set average are based on significantly lower numbers of samples.<sup>47</sup>

The concentration of mercury in coal also varies by geographic region from which the coal is mined. Based on the "best typical" values for each region, which are footnoted in Table 6-5, coals from the Appalachian and Gulf Provinces have the highest mean mercury concentration, 0.24 ppmwt for both regions. Also, based on the best available data, the lowest mean concentration is found in coals from the Alaska region (0.08 ppmwt). However, note that another study showed substantially higher levels (4.4 ppmwt). That study also showed that the greatest range of concentration is found in coals from the Alaska region with a reported range of 0.02 to 63 ppmwt.<sup>40</sup> The means reported in Table 6-5 may be regarded as typical in-ground concentrations of mercury in coals from each geographic region.

### 6.1.2 Process Description

As shown in Table 6-1, almost all coal combustion occurs in utility and industrial boilers. Almost all of the coal burned is bituminous and subbituminous (95 percent) and lignite (4 percent).<sup>40</sup> However, the processes used for the different coals are comparable. The paragraphs below first describe the boilers used for bituminous coal combustion. Then, lignite and anthracite combustion are described briefly. References 48 and 43 offer additional details on these processes.

The two major coal combustion techniques used to fire bituminous and subbituminous coals are suspension firing and grate firing. Suspension firing is the primary combustion mechanism in pulverized coal and cyclone systems. Grate firing is the primary mechanism in underfeed and overfeed stokers. Both mechanisms are employed in spreader stokers.

Pulverized coal furnaces are used primarily in utility and large industrial boilers. In these systems, the coal is pulverized in a mill to the consistency of talcum powder (i.e., at least 70 percent of the particles

TABLE 6-5. MERCURY CONCENTRATION IN COAL BY REGION

Region	No. of samples	Mercury concentration, ppmwt		
		Range	Arithmetic mean	Standard deviation
Appalachian	2,749	---	0.24 <sup>a</sup>	0.47
	331	<0.01-3.3	0.24 <sup>b</sup>	---
Interior	592	---	0.14 <sup>a</sup>	0.14
	155	0.01-0.83	0.14 <sup>b</sup>	---
	---	0.01-1.5	0.15	---
Illinois Basin <sup>c</sup>	82	0.03-1.6	0.21	0.22
	---	0.16-1.91	---	---
Gulf Province	38	---	0.24 <sup>a</sup>	0.19
	34	0.03-1.0	0.18 <sup>b</sup>	---
Northern Plains	371	---	0.11 <sup>a</sup>	0.10
	490	0.01-3.8	0.11	---
Rocky Mountains	184	---	0.09 <sup>a</sup>	0.12
	124	0.01-1.48	0.06 <sup>b</sup>	---
	---	0.01-8.0	0.11	---
Alaska	107	---	0.08 <sup>a</sup>	0.07
	18	0.02-63	4.4 <sup>b</sup>	---

Source: Reference 40.

<sup>a</sup> Values from Reference 41 are based on the most comprehensive data set currently available (the NCRDS) and may be used as typical values for mercury in coal from these regions.

<sup>b</sup> Values from Reference 42 are included in the NCRDS. Arithmetic means from the entire NCRDS are more representative than means from this study, since the NCRDS contains many more coal samples. The Reference 42 data are included to give an idea of the range of values for mercury content in individual coal samples from each region.

<sup>c</sup> Eastern section of Interior Province.

will pass through a 200-mesh sieve). The pulverized coal is generally entrained in primary air and suspension-fired through the burners to the combustion chamber. Pulverized coal furnaces are classified as either dry or wet bottom, depending on the ash removal technique. Dry bottom furnaces fire coals with high ash fusion temperatures, and dry ash removal techniques are used. In wet bottom (slag tap) furnaces, coals with low ash fusion temperatures are used, and molten ash is drained from the bottom of the furnace.

Cyclone furnaces burn low ash fusion temperature coal crushed to a 4-mesh size. The coal is fed tangentially, with primary air, to a horizontal cylindrical combustion chamber. Small coal particles are burned in suspension, while the larger particles are forced against the outer wall. Because of the high temperatures developed in the relatively small furnace volume, and because of the low fusion temperature of the coal ash, much of the ash forms a liquid slag that is drained from the bottom of the furnace through a slag tap opening. Cyclone furnaces are used mostly in utility and large industrial applications.

In spreader stokers, a flipping mechanism throws the coal into the furnace and onto a moving grate. Combustion occurs partially in suspension and partially on the grate. Because the entrained particles in the furnace exhaust have substantial carbon, fly ash reinjection from mechanical collectors is commonly used to improve boiler efficiency. Ash residue in the fuel bed is deposited in a receiving pit at the end of the grate.

In overfeed stokers, coal is fed onto a traveling or vibrating grate and burns on the fuel bed as it progresses through the furnace. Ash particles fall into an ash pit at the rear of the stoker. "Overfeed" applies because the coal is fed onto the moving grate under an adjustable gate. Conversely, in "underfeed" stokers, coal is fed upward into the firing zone by mechanical rams or screw conveyers. The coal moves in a channel, known as a retort, from which it is forced upward, spilling over the top of each side to feed the fuel bed. Combustion is completed by the time the bed reaches the side dump grates from which the ash is discharged to shallow pits.

The next most common coal used in the U.S. is lignite. Lignite is a relatively young coal with properties intermediate to those of bituminous coal and peat. Because lignite has a high moisture content (35

to 40 weight percent) and a low wet basis heating value (16,660 kJ/kg [7,190 Btu/lb]), it generally is used as a fuel only in areas in which it is mined. Lignite is used mainly for steam/electric production in power plants and typically is fired in larger pulverized coal-fired or cyclone-fired boilers.

Anthracite coal is a high-rank coal with more fixed carbon and less volatile matter than either bituminous coal or lignite. Because of its low volatile matter content and slight clinkering, anthracite is most commonly fired in medium-sized traveling grate stokers and small hand-fired units. Some anthracite (occasionally with petroleum coke) is used in pulverized coal-fired boilers, and it may be blended with bituminous coal. Because of its low sulfur content (typically less than 0.8 weight percent) and minimal smoking tendencies, anthracite is considered a desirable fuel in areas where it is readily available. In the United States, anthracite is mined primarily in northeastern Pennsylvania and consumed mostly in Pennsylvania and surrounding States. The largest use of anthracite is for space heating. Lesser amounts are employed for steam/electric production, typically in underfeed stokers and pulverized coal dry-bottom boilers.

Although small quantities of mercury may be emitted as fugitive particulate matter from coal storage and handling operations, the primary source of mercury and mercury compound emissions from coal combustion is the combustion stack. Because the combustion zone in boilers operates at temperatures in excess of 1100°C (2000°F), the mercury in the coal is vaporized and exits the combustion zone as a gas. As the combustion gases pass through the boiler and the air pollution control system, they cool, and some of the mercury and mercury compounds may condense on the surface of fine particles. The relative fractions of vapor- and particle-phase mercury in the exhaust stack depend primarily on the temperature of the air pollution control system, and the amount of residual carbon in the coal fly ash (some of the vaporous mercury and mercury compounds may adsorb onto carbon at temperatures present in some air pollution control devices). To date, little information has been obtained on these distributions.

### 6.1.3 Emission Control Measures

Emission control measures for coal-fired boilers include controls based on combustor design and operating practices that are directed primarily at nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) control and add-on air pollution control devices that are designed for acid gas and PM control.<sup>43</sup> Those measures that are most likely to affect mercury control are add-on control systems designed for both PM and acid gas control. The primary types of PM control devices used for coal combustion include multiple cyclones, electrostatic precipitators, fabric filters (baghouses), and wet scrubbers, while both wet and dry flue gas desulfurization (FGD) systems are used for sulfur dioxide (SO<sub>2</sub>). Some measure of PM control is also obtained from ash settling in boiler/air heater/economizer dust hoppers, large breeches and chimney bases, but these mechanisms will not reduce mercury emissions.

Electrostatic precipitators (ESP) are the most common high efficiency control devices used on pulverized coal and cyclone units. These devices are also being used increasingly on stokers. Generally, PM collection efficiencies are a function of the specific collection area (i.e., the ratio of the collection plate area per volumetric flow rate of flue gas through the device). Particulate matter efficiencies of 99.9 weight percent have been measured with ESP's. Fabric filters have recently seen increased use in both utility and industrial applications both as a PM control measure and as the collection mechanism in dry FGD systems, generally achieving about 99.8 percent PM control. Wet scrubbers are also used to control PM emissions, although their primary use is to control emissions of sulfur oxides. Because, unlike the other PM control devices, wet scrubbers reduce the gas stream temperature, they may be more effective than the other controls in removing condensable PM, such as mercury. The other PM control devices would require some type of acid gas control, such as a spray dryer.

Mechanical collectors, generally multiple cyclones, are the primary means of control on many stokers and are sometimes installed upstream of high efficiency control devices in order to reduce the ash collection burden. Depending on application and design, multiple cyclone PM efficiencies can vary tremendously. However, these systems are relatively inefficient for fine particles and are not likely to provide measurable control of mercury emissions, which are primarily in the vapor and fine particle fractions of the exhaust.

The section on emissions below presents the available data on emission control system performance. However, in evaluating the potential emissions from a facility or group of facilities, any assumptions about control system performance, including those based on the data presented herein, should be examined carefully to assure that they are supported by reliable test data obtained via methods comparable to those described in Section 9. Also, performance estimates must be consistent with the physical and chemical properties of the compounds being emitted and with the operating characteristics of the systems being evaluated.



#### 6.1.4 Emissions

This revision of the coal-fired boiler section of the previous mercury L&E document presents separate sections for utility boilers and commercial/industrial/residential coal-fired boilers.<sup>32</sup> Since the previous mercury L&E document was published in 1993, EPA conducted a comprehensive study to estimate hazardous air pollutant (HAP) emissions, including mercury, from utility boilers.<sup>46</sup> The results of this study were published in a report covering trace metal, organic HAP, and radionuclide emissions; control techniques from utility boilers; and a comprehensive risk assessment.<sup>46</sup> Additionally, a brief description and presentation of the results of the study specifically with respect to mercury emissions and controls was published in the Mercury Study Report to Congress.<sup>33</sup> These EPA reports quantified the impact on mercury emissions from coal-fired utility boilers of both coal cleaning and existing combinations of boilers and control devices. The reports included data from multiple emission test programs and represent the most comprehensive mercury emission estimates available for coal-fired utility boilers. Therefore, the approach described in these documents for coal-fired utility boilers has been adopted for this document. For commercial/industrial/residential coal-fired boilers, the approach adopted in the previous mercury document (EPA, 1993) is relatively unchanged.<sup>32</sup>

In providing comments on the draft of this L&E document, EPRI suggested that EPA use the results of the EPRI report, *Mercury and Other Trace Metals in Coal*, to develop mercury emission estimates from coal combustion.<sup>49</sup> This report presented the results of the analysis of 154 coal samples from full-scale power plants. These results were also available in Reference 47. For bituminous coal, an average mercury concentration of 0.087 ppm is reported, a level more than 50 percent lower than the 0.21 ppm average concentration for the USGS data set. EPRI considers the data presented in Reference 49 to be of better quality than the USGS data set because of the use of more accurate sampling and analytical techniques.<sup>50</sup> Additionally, EPRI asserts that the 154 samples are "coal-as-burned" samples versus those in the USGS data set that include samples from coal seams containing "significant levels of noncombustibles and uneconomic samples."<sup>50</sup>

For the purposes of this L&E document, it was important that the mercury emission estimates be consistent with mercury emission estimates developed by other groups within EPA. Therefore, for agency consistency, and, as described in this section of the L&E document, the mercury emission estimates presented reflect those developed in the Utility HAP study. While EPA does not dispute the validity of the mercury in coal data in Reference 51, these data were not included in the development of the mercury emission estimates presented in the Utility HAP study and, therefore, are not included in the mercury emission estimates presented in this section. However, these data may be included in the revised Utility HAP study that is expected to be released in early 1998. For now, the estimates presented in section 6.1.4 reflect EPA's position on mercury emission estimates from coal combustion.

**6.1.4.1 Utility Boilers.** The approach used to develop mercury emission estimates in the Utility HAP study comprised a two-step process.<sup>32,33</sup> First, the mercury concentration in the coal was estimated. Then, using the boiler-specific data in the Utility Data Institute (UDI)/Edison Electric Institute (EEI) Power Statistics data base (1991 edition), the estimated mercury concentration in the fuel was multiplied by the fuel feed rate to obtain the total amount of mercury entering each boiler listed in the data base. Second, "emission modification factors" (EMF's) were developed based on test data that represent the level of mercury control that could be expected across various boiler configurations and control devices. The EMF's developed from the tested units were applied to all other similar units to give mercury emission estimates on a per-unit basis.<sup>32,33</sup>

The estimates of mercury concentrations in coal were developed by using a USGS data base of trace element concentrations in coal by State of coal origin for 3,331 core and channel samples of coal. These samples came from 50 coal beds having the highest coal production in the United States. The average mercury content of each of these beds was calculated and the location of each bed was matched with a State. Using the UDI/EEI data base and records of actual coal receipts, the State from which each utility purchased the majority of its coal was identified. Then, the mercury content of the coal fired by each utility was assigned based on the average concentration of mercury calculated for each coal bed.<sup>32,33</sup>

To account for the impact of coal cleaning on mercury concentration in coal, a 21 percent reduction in mercury concentration was attributed to coal cleaning for those boilers purchasing bituminous coal from States where coal cleaning is common practice.<sup>32,33</sup> While approximately 77 percent of the eastern and midwestern bituminous coals are cleaned, the 21 percent reduction was assumed for all boilers burning

bituminous coal east of the Mississippi River.<sup>51</sup> No coal cleaning reductions were applied to lignite or subbituminous coals, or bituminous coal when the State of coal origin was west of the Mississippi River.<sup>32,33</sup>

The mercury input to each boiler in the data base was calculated by multiplying the boiler feed rate by the mercury content in the assigned coal and assessing the 21 percent reduction attributed to coal cleaning, as appropriate.<sup>32,33</sup>

Emissions data were available from 51 emission tests conducted by the U.S. EPA, the Electric Power Research Institute (EPRI), the Department of Energy (DOE), and individual utilities. The EMF's were calculated from the emission test data by dividing the amount of mercury exiting either the boiler or control device by the amount of mercury entering the boiler. Boiler-specific emission estimates were then calculated by multiplying the calculated inlet mercury input by the appropriate EMF for each boiler configuration and control device. The utility emission test data are listed in Section 10 of the Utility HAP study and in Appendix B of the U.S. EPA Mercury Report to Congress.<sup>33</sup> The EMF's for the various boiler configurations and control devices are shown in Appendix C of the Utility HAP study and in Appendix C of the U.S. EPA Mercury Report to Congress.<sup>33,46</sup>

To calculate the mercury emissions from a specific boiler, the following equation was used:

$$\left( \begin{array}{c} \text{Mercury} \\ \text{emissions} \end{array} \right) = \left( \begin{array}{c} \text{Mercury} \\ \text{content} \\ \text{in coal} \end{array} \right) \times \left( \begin{array}{c} \text{Boiler} \\ \text{feed rate} \end{array} \right) \times \left( \begin{array}{c} \text{Coal} \\ \text{cleaning} \\ \text{factor} \end{array} \right) \times \left( \begin{array}{c} \text{EMF} \end{array} \right)$$

For boilers burning bituminous coal when the State of coal origin was east of the Mississippi River, a coal cleaning factor of 0.79 (reflecting a mercury reduction of 21 percent) was applied to the above equation. For all other boilers in the data base, no coal cleaning reductions were applied, i.e., in the above equation, the coal cleaning factor for these boilers was equated to one. The results of applying this operation to the boilers in the data base indicate that the total nationwide mercury emissions from coal-fired utility boilers are approximately 51 ton/yr or 46.3 Mg/yr.<sup>33</sup>

**6.1.4.2 Commercial/Industrial/Residential Boilers.** For commercial/industrial/residential boilers, the data presented above on mercury concentrations in coal and coal heating values were used to develop mass balance-based emission factors.

The information presented in the literature indicates that virtually 100 percent of the mercury contained in the coal is emitted from the furnace as either a vapor or fine PM. Consequently, the coal heating values presented in Table 6-2 and the coal mercury concentrations presented in Table 6-4 can be used to develop uncontrolled emission factors for major coal types under the conservative assumption that all mercury in the coal is emitted. Furthermore, note that the coal composition data in Table 6-4 are based on in-ground mercury concentrations and that calculated emission factors shown in Table 6-6 are based on the conservative assumption that as-fired coal contains equivalent concentrations. The emission factors do not account for coal washing. To account for coal washing, a mercury emission reduction of 21 percent can be applied to the factors in Table 6-6.

The uncontrolled emission factors listed in Table 6-6 were calculated using the coal heating values from Table 6-2 and the coal mercury concentrations in Table 6-4. These calculated emission factors were compared with the latest emission factors for coal combustion published in AP-42.<sup>52,53</sup> In AP-42, separate emission factors were developed for bituminous/subbituminous and for anthracite coal combustion based on available emission test data. For bituminous/subbituminous coal, the AP-42 uncontrolled emission factor is 16 lb/10<sup>12</sup> Btu and has an E rating. This factor is identical to the calculated uncontrolled emission factor for bituminous coal presented in Table 6-6. For anthracite coal combustion, the AP-42 uncontrolled

TABLE 6-6. CALCULATED UNCONTROLLED MERCURY EMISSION FACTORS  
FOR COAL COMBUSTION

Coal type	Calculated mercury emission factors			
	kg/10 <sup>15</sup> J	lb/10 <sup>12</sup> Btu	g/Mg coal	10 <sup>-3</sup> lb/ton coal
Bituminous <sup>a</sup>	7.0	16	0.21	0.42
Subbituminous <sup>b</sup>	4.5	10	0.10	0.20
Anthracite <sup>c</sup>	7.6	18	0.23	0.46
Lignite <sup>d</sup>	9.0	21	0.15	0.30

<sup>a</sup>Based on arithmetic average of the five average heating values in Table 6-2.

<sup>b</sup>Based on arithmetic average of the three average heating values in Table 6-2.

<sup>c</sup>Based on average heating value for coal category A2 in Table 6-2.

<sup>d</sup>Based on average heating value for coal category L1 in Table 6-2.

emission factor is 0.13 x 10<sup>-3</sup> lb/ton of coal and also has an E rating. This factor, while smaller than the calculated value for anthracite coal (0.46 x 10<sup>-3</sup> lb/ton of coal) presented in Table 6-6, is of the same order of magnitude as the calculated value. The AP-42 did not present a separate emission factor for lignite coal combustion. The emission factors presented in Table 6-6 are considered to be better factors to use in developing nationwide mercury emission estimates than the AP-42 factors for the following reasons. The two AP-42 emission factors were developed using limited data while the calculated uncontrolled emission factors represent a significant volume of mercury-concentration-in-coal data. Calculated uncontrolled factors were developed for each coal type while the AP-42 emission factors were developed only for bituminous/subbituminous and anthracite coals.

A comprehensive summary of the test data generated prior to 1989 for coal-fired boilers and furnaces is presented in Reference 40. The data from individual tests that are presented in that report are compiled in Table B-1 in Appendix B of Reference 54. Table 6-7 summarizes these data as a function of coal type and control status. Note the wide range of emission factors for each coal type. In addition to the variability in coal heat content and the uncertainty in mercury sampling and analysis, this range reflects the substantial variation in coal mercury content and highlights the need to obtain coal-specific mercury data to calculate emission estimates whenever possible. Also note that the data are combined across industry sector and boiler type because these parameters are not expected to have a substantial effect on emission factors.

The test data summarized in Table 6-7 from Reference 40, although limited, indicate that essentially no control of mercury in flue gas is achieved by multiclones, up to 50 percent control is achieved by ESP's, and limited scrubber data show mercury efficiencies of 50 and 90 percent. Long-term scrubber performance will depend on the blowdown rate for the scrubber, with efficiency falling if the system approaches equilibrium. However, according to literature references discussed in Reference 40, these control efficiencies may be biased high because they are based on data collected using older test methods, which tended to collect mercury vapor inefficiently. Consequently, these estimates represent upper bounds of efficiencies. More information on the methods for sampling and analysis of mercury in flue gas is presented in Section 9.

The test data reported in the Utility HAP study comprises data that was collected using more up to date test methods. This study reported the following mercury control efficiencies for individual control devices controlling emissions from coal-fired utility boilers: 0 to 59 percent for FGD systems (6 tests); 0 percent control for hot-side ESP's (ESP's located upstream of an FGD unit) (2 tests); zero to 82 percent control for cold-side ESP's (17 tests); zero to 73 percent control for fabric filters (5 tests); and zero to 55 percent control for spray dryer absorber/fabric filter (SDA/FF) systems (4 tests).

Based on review of the available data, the best estimates for uncontrolled emission factors for typical coal combustion facilities are those obtained from a mass balance using coal composition data. This approach was selected because the available uncontrolled test data for commercial/industrial/

TABLE 6-7. MEASURED MERCURY EMISSION FACTORS FOR COAL COMBUSTION

Coal type <sup>a</sup>	Control status <sup>b</sup>	No. of boilers	No. of data points	Measured mercury emission factors							
				kg/10 <sup>15</sup> J		lb/10 <sup>12</sup> Btu		g/Mg coal <sup>d</sup>		10 <sup>-3</sup> lb/ton coal <sup>e</sup>	
				Mean	Range <sup>c</sup>	Mean	Range <sup>c</sup>	Mean	Range <sup>c</sup>	Mean	Range <sup>c</sup>
B <sup>d</sup>	UN	17	34	3.8	0.005-133	8.8	0.011-308	0.11	0.00015-4.0	0.23	0.00029-8.0
B <sup>d</sup>	MP or MC	9	15	12.9	0.60-77	29.9	1.4-180	0.39	0.018-2.3	0.78	0.036-4.7
B <sup>d</sup>	ESP or MP/ESP	29	59	3.4	0.18-9.6	8.0	0.41-22.3	0.10	0.0055-0.29	0.21	0.011-0.58
B <sup>d</sup>	ESP-2 stage	1	5	0.086	0.005-0.25	0.20	0.011-0.56	0.0026	0.00015-0.0075	0.0052	0.00029-0.015
B <sup>d</sup>	WS or MC/WS	5	5	7.9	b.d.-37	18.4	b.d.-86	0.24	b.d.-1.1	0.48	b.d.-2.2
B <sup>d</sup>	FF	1	1	2.0	--	4.6	--	0.060	--	0.12	--
SB <sup>e</sup>	UN	3	5	13.0	0.28-35	30.2	0.64-81	0.29	0.0062-0.78	0.58	0.012-1.5
SB <sup>e</sup>	ESP or MP/ESP	3	5	1.2	0.16-1.8	2.7	0.37-4.1	0.027	0.0035-0.040	0.052	0.0071-0.078
SB <sup>e</sup>	WS	2	2	3.4	2.1-4.7	8.0	4.9-11	0.075	0.047-0.10	0.15	0.094-0.21
L <sup>f</sup>	MC	4	4	4.1	1.9-9.5	9.6	4.4-22	0.068	0.032-0.16	0.14	0.063-0.32
L <sup>f</sup>	ESP	3	3	0.18	0.099-0.23	0.41	0.23-0.53	0.0030	0.0016-0.0038	0.0059	0.0033-0.0076
A <sup>g</sup>	UN	3	3	2.3	1.5-3.0	5.3	3.5-7.0	0.070	0.045-0.091	0.14	0.091-0.18

Source: Reference 40.

<sup>a</sup>B = bituminous, SB = subbituminous, L = lignite, A =anthracite.<sup>b</sup>UN = uncontrolled, MP = mechanical precipitation system, MC =multiclone, ESP = electrostatic precipitator, WS =wet scrubber.<sup>c</sup>b.d. = below detection limits.<sup>d</sup>Based on arithmetic average of the five average heating values in Table 6-2.<sup>e</sup>Based on arithmetic average of the three average heating values in Table 6-2.<sup>f</sup>Based on average heating value for coal category L1 in Table 6-2.<sup>g</sup>Based on average heating value for coal category A2 in Table 6-2.

residential boilers are of uncertain quality, and the coal concentration data are representative of a much larger industry segment. Utilizing the available data from Reference 40, and the Utility HAP's study, controlled emission factors were obtained by applying the following percent removal efficiencies to the uncontrolled emission factors in Table 6-6. Zero percent efficiency for mechanical collectors, 0 to 82 percent control for ESP's, 0 to 60 percent control for wet scrubbers and FGD systems, 0 to 73 percent for fabric filters, and 0 to 55 percent for SDA/FF systems. The resultant best typical emission factors are shown in Table 6-8.

The mercury emission factors presented in Table 6-8 should be viewed as the most realistic nationwide estimates possible, based on the little data that are available. It should be recognized that there is considerable uncertainty in these estimates. The uncertainty in the estimates is due to the wide variability in mercury concentrations in coal, the variability in coal heat content, and the uncertainty in sampling and analytical methodologies for detecting mercury. Therefore, these estimates should not be used to determine emissions from specific coal combustion facilities.

Estimates of the total 1994 nationwide mercury emissions from coal-fired commercial/industrial/residential boilers are 21.5 Mg (23.6 tons); for additional details, see Appendix A. The total 1994 nationwide mercury emission estimates for coal combustion (utility plus commercial/industrial/residential) are 67.8 Mg (74.6 tons).

## 6.2 FUEL OIL COMBUSTION

As shown in Table 6-1, based on energy consumption estimates by the U.S. Department of Energy, fuel oil use spans the four sectors of energy users. Distillate fuel oil is used in all sectors with the largest use in the residential (35 percent) and the industrial (43 percent) sectors, but also with amounts used in both the commercial (18 percent) and utility (4 percent) sectors. Residual oil is used primarily in the industrial (29 percent) and utility (59 percent) sectors. Because the oil combustion process is not complex, and control systems are not widely applied to oil-fired units, the discussion below will focus on fuel characteristics and on emissions from oil-fired units.<sup>39</sup>

### 6.2.1 Fuel Oil Characteristics

The fuel oil characteristics of greatest importance for characterizing mercury emissions from fuel oil combustion are the heating value and the mercury content of the oil. The heating value is used for converting from emission factors with mass- or volume-based activity levels to those with activity levels based on heat input.

The term fuel oil covers a variety of petroleum products, including crude petroleum, lighter petroleum fractions such as kerosene, and heavier residual fractions left after distillation.<sup>40</sup> To provide standardization and means for comparison, specifications have been established that separate fuel oils into various grades. Fuel oils are graded according to specific gravity and viscosity, with No. 1 Grade being the lightest and No. 6 the heaviest. The heating value of fuel oils is expressed in terms of kJ/L (Btu/gal) of oil at 16°C (60°F) or kJ/kg (Btu/lb) of oil. The heating value per gallon increases with specific gravity because there is more weight per gallon. The heating value per mass of oil varies inversely with specific gravity because lighter oil contains more hydrogen. For an uncracked distillate or residual oil, heating value can be approximated by the following equation:

$$\text{Btu/lb} = 17,660 + (69 \times \text{API gravity})$$

For a cracked distillate, the relationship becomes:

$$\text{Btu/lb} = 17,780 + (54 \times \text{API gravity})$$

Table 6-9 provides an overall summary of the heating values of typical fuel oils used in the U.S., and Table 6-10 shows the variability in fuel oil heating values used in various regions of the country. Appendix B of Reference 40 provides additional details.

The data base for mercury content in fuel oils is much more limited than the coal mercury content data base. A number of petroleum industry associations were contacted, but none who responded have

TABLE 6-8. BEST TYPICAL MERCURY EMISSION FACTORS FOR COMMERCIAL/INDUSTRIAL/RESIDENTIAL COAL-FIRED BOILERS

Coal type <sup>a</sup>	Control status <sup>b</sup>	Typical mercury emission factors			
		kg/10 <sup>15</sup> J	lb/10 <sup>12</sup> Btu	g/Mg coal	10 <sup>-3</sup> lb/ton coal
B	Uncontrolled	7.0	16	0.21	0.42
B	Mechanical collector	7.0	16	0.21	0.42
B	ESP	1.3-7.0	2.9-16	0.038-0.21	0.08-0.42
B	WS/FGD	0.7-7.0	1.6-16	0.021-0.21	0.042-0.42
B	FF	1.9-7.0	4.3-16	0.012-0.21	0.11-0.42
B	SDA/FF	3.2-7.0	7.2-16	0.095-0.21	0.19-0.42
SB	Uncontrolled	4.5	10	0.10	0.20
SB	Mechanical collector	4.5	10	0.10	0.20
SB	ESP	0.81-4.5	0.18-10	0.018-0.10	0.036-0.020
SB	WS/FGD	0.4-4.5	1-10	0.010-0.10	0.02-0.20
SB	FF	1.2-4.5	2.7-10	0.027-0.10	0.05-0.20
SB	SDA/FF	2.0-4.5	4.5-10	0.045-0.10	0.09-0.20
A	Uncontrolled	7.6	18	0.23	0.46
A	Mechanical collector	7.6	18	0.23	0.46
A	ESP	1.4-7.6	3.2-18	0.04-0.23	0.08-0.46
A	WS/FGD	0.7-7.6	1.8-18	0.023-0.23	0.046-0.46
A	FF	2.1-7.6	4.9-18	0.06-0.23	0.12-0.46
A	SDA/FF	3.4-7.6	8.1-18	0.10-0.23	0.21-0.46
L	Uncontrolled	9.0	21	0.15	0.30
L	Mechanical collector	9.0	21	0.15	0.30
L	ESP	1.6-9.0	3.8-21	0.03-0.15	0.05-0.30
L	WS/FGD	0.9-9.0	2.1-21	0.015-0.15	0.030-0.30
L	FF	2.4-9.0	5.7-21	0.04-0.15	0.08-0.30
L	SDA/FF	4.1-9.0	9.5-21	0.07-0.15	0.14-0.30

Source: Reference 32.

<sup>a</sup>B = bituminous, SB = subbituminous, A = anthracite, L = lignite.

<sup>b</sup>ESP = electrostatic precipitator, WS/FGD = wet scrubber or flue gas desulfurization system, FF = filter fabric, and SDA/FF = spray dryer absorber/fabric filter system.

TABLE 6-9. TYPICAL HEATING VALUES OF FUEL OILS

	FUEL OIL GRADES					
	No. 1	No. 2	No. 4	No. 5	No. 6	
Type	Distillate	Distillate	Very light residual	Light residual	Residual	Crude
Color	Light	Amber	Black	Black	Black	
Heating value <sup>a</sup>						
kJ/L	38,200	40,900	40,700	41,200	41,800	40,000-42,300
(Btu/gal)	(137,000)	(141,000)	(146,000)	(148,000)	(150,000)	(144,000-152,000)
kJ/kg	45,590-46,030	44,430-45,770	42,370-44,960	41,950-44,080	40,350-43,800	40,700-43,300
(Btu/lb)	(19,670-19,860)	(19,170-19,750)	(18,280-19,400)	(18,100-19,020)	(17,410-18,900)	(17,500-18,600)

Source: Reference 40; and Reference 54.

<sup>a</sup> The distillate samples, as well as the residual samples, analyzed for Btu/gal and Btu/lb heating values are different; therefore, the heating values presented do not directly correspond to one another.

<sup>b</sup> These crude oil values are based on a limited number of samples from West Coast field sites presented in Reference 55 and may not be representative of the distribution of crude oils processed in the United States.

TABLE 6-10. TYPICAL FUEL OIL HEATING VALUES FOR SPECIFIC REGIONS

Region	No. 1 fuel oil			No. 2 fuel oil			No. 4 fuel oil		
	Heating value, kJ/L (Btu/gal)								
	No. of samples	Range	Average	No. of samples	Range	Average	No. of samples	Range	Average
Eastern	33	36,900-37,800 (132,500-135,700)	37,400 (134,200)	56	37,100-40,800 (133,100-146,600)	38,800 (139,500)	1	--- ---	40,700 (146,000)
Southern	13	37,000-37,700 (132,900-135,400)	37,400 (134,300)	19	38,000-39,400 (136,400-141,500)	38,800 (139,400)	0	--- ---	--- ---
Central	27	36,900-37,800 (132,500-135,700)	37,300 (134,000)	35	37,800-40,800 (135,900-146,600)	38,800 (139,200)	2	40,700-41,800 (146,000-150,100)	41,200 (148,000)
Rocky Mountain	14	37,100-37,600 (133,100-135,100)	37,400 (134,200)	17	37,900-39,100 (136,100-140,400)	38,700 (139,000)	2	41,800-41,900 (150,100-150,500)	41,900 (150,300)
Western	16	36,700-37,900 (131,700-136,200)	37,500 (134,600)	18	37,900-39,100 (136,100-140,500)	38,700 (139,000)	0	--- ---	--- ---

Region	No. 5 fuel oil (light)			No. 6 fuel oil		
	Heating value, kJ/L (Btu/gal)					
	No. of samples	Range	Average	No. of samples	Range	Average
Eastern	1	---	41,300 (148,400)	17	40,900-43,900 (147,000-157,600)	43,300 (151,900)
Southern	0	---	---	14	41,900-43,600 (150,500-156,500)	42,600 (152,900)
Central	4	41,300-42,200 (148,400-151,500)	41,700 (149,900)	10	41,900-44,200 (150,600-158,900)	42,600 (152,900)
Rocky Mountain	2	42,900-43,600 (153,900-156,500)	43,200 (155,200)	7	42,300-44,300 (151,900-159,200)	43,100 (154,600)
Western	0	---	---	12	41,700-45,500 (149,900-163,500)	43,000 (154,400)

Source: Reference 40.



done any research on metals content in fuel oils. No single centralized data base is available, and the information presented below is based on limited data from individual studies.

Concentrations of mercury in fuel oil depend upon the type of oil used. No comprehensive oil characterization studies have been done, but data in the literature report mercury concentrations in crude oil ranging from 0.023 to 30 ppmwt, while the range of concentrations in residual oil is 0.007 to 0.17 ppmwt. Because only a single mean value was found in the literature for mercury concentration in distillate oil, no conclusions can be drawn about the range of mercury in distillate oil. Table 6-11 lists typical values for mercury in oils, which were obtained by taking the average of the mean values found in the literature. The value for distillate oil is the single data point found in the literature and may not be as representative as the values for residual and crude oils.

TABLE 6-11. MERCURY CONCENTRATION IN OIL BY OIL TYPE

Fuel oil type	No. of samples	Mercury concentration, ppmwt	
		Range	Typical value
Residual No. 6	--	0.002-0.006	0.004 <sup>a</sup>
Distillate No. 2	--	--	<0.12 <sup>b</sup>
Crude	46	0.007-30	3.5 <sup>c</sup>

Source: References 40, 50, 56.

<sup>a</sup>Midpoint of the range of values.

<sup>b</sup>Average of data from three sites.

<sup>c</sup>Average of 46 data points was 6.86; if the single point value of 23.1 is eliminated, average based on 45 remaining data points is 1.75. However, the largest study with 43 data points had an average of 3.2 ppmwt. A compromise value of 3.5 ppmwt was selected as the best typical value.

### 6.2.2 Process Description

Fuel oils are broadly classified into two major types: distillate and residual. Distillate oils (fuel oil grade Nos. 1 and 2) are more volatile and less viscous than residual oils, having negligible ash and nitrogen contents and usually containing less than 0.1 weight percent sulfur. No. 4 residual oil is sometimes classified as a distillate; No. 6 is sometimes referred to as Bunker C. Being more viscous and less volatile than distillate oils, the heavier residual oils (Nos. 5 and 6) must be heated to facilitate handling and proper atomization. Because residual oils are produced from the residue after lighter fractions (gasoline and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur. Small amounts of crude oil are sometimes burned for steam generation for enhanced oil recovery or for refinery operations.<sup>43,48</sup>

Oil-fired boilers and furnaces are simpler and have much less variation in design than the coal-fired systems described earlier. The primary components of the system are the burner, which atomizes the fuel and introduces it along with the combustion air into the flame, and the furnace, which provides the residence time and mixing needed to complete combustion of the fuel. The primary difference in systems that fire distillate oil and residual oil is that the residual oil systems must have an oil preheater to reduce the viscosity of the oil so that it can be atomized properly in the burner. Systems that fire distillate oil and residual oil also have different atomization methods.

The only source of mercury emissions from oil-fired boilers and furnaces is the combustion stack. Because the entire fuel supply is exposed to high flame temperatures, essentially all of the mercury and mercury compounds contained in the fuel oil will be volatilized and exit the furnace with the combustion gases. Unless these combustion gases are exposed to low-temperature air pollution control systems and high-efficiency PM control systems, which typically are not found on oil-fired units, the mercury and mercury compounds will be exhausted in vapor phase through the combustion stack.

### 6.2.3 Emission Control Measures

The three types of control measures applied to oil-fired boilers and furnaces are boiler modifications, fuel substitution, and flue gas cleaning systems.<sup>40,48</sup> Only fuel substitution and flue gas cleaning systems may affect mercury emissions. Fuel substitution is used primarily to reduce SO<sub>2</sub> and NO<sub>x</sub> emissions. However, if the substituted fuels have lower mercury concentrations, the substitution will also reduce mercury emissions. Because PM emissions from oil-fired units are generally much lower than those from coal-fired units, high-efficiency PM control systems are generally not employed on oil-fired systems. However, the flue gas cleaning systems that are used on oil-fired units are described briefly below.

Flue gas cleaning equipment generally is employed only on larger oil-fired boilers. Mechanical collectors, a prevalent type of control device, are primarily useful in controlling PM generated during soot blowing, during upset conditions, or when a very dirty heavy oil is fired. During these situations, high efficiency cyclonic collectors can achieve up to 85 percent control of PM, but negligible control of mercury is expected with mechanical collectors.

Electrostatic precipitators are used on approximately one-third of the oil-fired power plants. Older ESP's may remove 40 to 60 percent of the PM, but negligible mercury control is expected. Newer ESP's may be more efficient, but no data are available for oil-fired power plants. Recent test data indicate mercury control efficiencies for ESP's controlling emissions from oil-fired utility boilers of 42 and 83 percent.<sup>46</sup> Scrubbing systems have been installed on oil-fired boilers to control both sulfur oxides and PM. Similar to systems applied to coal combustion (presented in Reference 40), these systems can achieve PM control efficiencies of 50 to 90 percent. Because they provide gas cooling, some mercury control may be obtained, but little data are available on their performance.

### 6.2.4 Emissions

The only substantive source of mercury emissions from fuel oil combustion operations is the combustion gas exhaust stack. Three types of information were used to develop emission factors for oil combustion. First, the data described above on fuel oil heating value and mercury content of fuel oils were used to develop emission factors by mass balance, assuming conservatively that all mercury fired with the fuel oil is emitted through the stack. Second, the emission factors developed in AP-42 for residual and distillate oil combustion and in Reference 47 for residual oil combustion were evaluated. Third, rated emission test data were evaluated and summarized. The paragraphs below first present the results generated from each of the three sources. Then, the relative merits of the emission factors generated via each of the procedures are discussed, and the best "typical" emission factors are identified.

The literature on fuel oil combustion suggests that essentially all mercury in the fuel oil is vaporized in the combustion zone and exhausted as a vapor in the combustion gas stream. Using the assumption that 100 percent of the mercury in fuel oil leaves the boiler or furnace in the exhaust gases, the data in Tables 6-9 and 6-11 were used to calculate uncontrolled emission factors for No. 2 distillate and No. 6 residual oil. Data presented in Reference 52, which show average crude oil heating values of 42,500 kJ/kg (18,300 Btu/lb) and 41,300 kJ/L (148,000 Btu/gal), can be combined with the mercury content data in Table 6-11 to calculate uncontrolled emission factors for crude oil combustion. The results of these calculations are presented in Table 6-12.

The calculated emission factors in Table 6-12 were compared to the available emission factors for fuel oil combustion from AP-42. The AP-42 presents emission factors for No. 2 and No. 6 fuel oils; no emission factors are developed for crude oil in AP-42.<sup>53</sup> The AP-42 emission factor for residual oil (No. 6) combustion is based on emission tests from 15 sites conducted from April 1990 through April 1994. The average emission factor reported for mercury emissions is 1.13 E-04 lb/10<sup>3</sup> gallons (0.73 lb/10<sup>12</sup> Btu). This emission factor is rated C. The comparable calculated emission factor for residual oil in Table 6-12 based on the mercury content in the oil is 3.3 E-05 lb/10<sup>3</sup> gallons (0.21 lb/10<sup>12</sup> Btu).

The AP-42 emission factor for distillate oil (No. 2) combustion (3.0 lb/10<sup>12</sup> Btu) is actually based on the average concentration of mercury in residual oil.<sup>40</sup> It is not based on any emission test data and is rated E. Additionally, the residual oil mercury concentration data used to develop this estimate are somewhat dated. The comparable calculated emission factor for distillate oil in Table 6-12 is 6.2 lb/10<sup>12</sup>

TABLE 6-12. CALCULATED UNCONTROLLED MERCURY EMISSION FACTORS  
FOR FUEL OIL COMBUSTION

Fuel oil type	Calculated mercury emission factors					
	kg/10 <sup>15</sup> J	lb/10 <sup>12</sup> Btu	g/Mg fuel oil	10 <sup>-3</sup> lb/ton fuel oil	g/10 <sup>3</sup> L fuel oil	lb/10 <sup>6</sup> gal fuel oil
Residual No. 6 <sup>a</sup>	0.092	0.21	0.004	0.008	0.0039	0.033
Distillate No. 2 <sup>a</sup>	2.7	6.2	0.12	0.24	0.10	0.86
Crude <sup>b</sup>	82	190	3.5	7.0	3.4	28

<sup>a</sup>Based on typical heating values in Table 6-9 and mercury concentrations in Table 6-11.

<sup>b</sup>Based on average crude oil heating values in Reference 54 and mercury concentrations in Table 6-11.

Btu and is based on the average of the mercury concentration measured in distillate oil samples at three sites as part of the California AB2588 study.<sup>50</sup>

Reference 40 contains some mercury emission test data for the combustion of residual oil, distillate oil, and a 1:1 mixture of residual/crude oil. All of these data were developed from 1979 through 1981 and were presented in the previous mercury L&E. In an effort to eliminate mercury emission test data collected using older, less reliable emission test methods, EPA elected to utilize only post-1990 emission test data. This approach is consistent with the approach utilized in EPA's Utility HAP Study. Therefore, the emission test data from Reference 40 are not utilized here; instead, more recent test data are presented.

Table 6-13 presents the results of a series of emission tests for the combustion of residual oil reported in Reference 47. As part of this test program, residual oil mercury concentrations were also measured; these data are also presented in Table 6-13. The data show that the mercury emissions from residual oil combustion are highly variable and that in most cases, the measured stack emissions are higher than the inlet fuel levels. Because these data are not normally distributed and appear to be log normal, a geometric mean was calculated to better represent the range of the data (References 47 and 56). The geometric mean for these data is 0.46 lb/10<sup>12</sup> Btu. Data are not available for distillate or crude oil combustion in Reference 47.

In summary, three mercury emission factors are presented for residual oil combustion: the 0.73 lb/10<sup>12</sup> Btu factor from AP-42, 0.46 lb/10<sup>12</sup> Btu from EPRI, and 0.21 lb/10<sup>12</sup> Btu from the EPRI residual oil analyses. Because the 0.46 lb/10<sup>12</sup> Btu emission factor is essentially the midpoint of the range of the three values, this factor was selected as the best "typical" emission factor for residual oil combustion. Because there are no emission test data for distillate oil combustion, the mass balance approach was used to estimate the best "typical" emission factor for distillate oil combustion.

As a part of the previous L&E study, two test reports prepared as a part of the California "Hot Spots" program were reviewed.<sup>54,57</sup> The emission factors generated from these three reports are summarized in Table 6-14. Each of the reports contained the data on fuel oil characteristics needed to calculate mercury input rates, so Table 6-14 contains both calculated emission factors based on mercury input levels and measured emission factors based on stack tests. Because mercury levels in all of the fuel oils tested were below detection limits, all calculated emission factors are reported as "less than" values. Note that only one of the two tests showed mercury levels above the detection limit in the stack. That test showed measured emissions to be substantially greater than mercury input to the process, making the results suspect. These discrepancies may be a function of the analytical problems that have been reported for mercury methods applied to combustion sources. These problems are discussed in more detail in Section 9. On balance, these data provide little information for emission factor development.

The available information on uncontrolled mercury emissions from crude oil combustion is ambiguous. The limited test data presented in Table 6-14 show measured factors that range from less than 0.05 to 15 kg/10<sup>15</sup> J (<0.12 to 34 lb/10<sup>12</sup> Btu), a range of almost three orders of magnitude. The calculated emission factor of 84 kg/10<sup>15</sup> J (190 lb/10<sup>12</sup> Btu), which is based on limited fuel composition

TABLE 6-13. MERCURY CONCENTRATIONS IN RESIDUAL OIL AND MERCURY EMISSION FACTORS FROM RESIDUAL COMBUSTION

Unit name	Residual oil mercury concentration, ppmw	Mean mercury emission factor, lb/10 <sup>12</sup> Btu
117	0.0023	0.60
118	0.0040	0.98
112	0.0060	1.3
13	<0.040	0.23
103	<0.090	<3.6
106	<0.10	<5.0
107	<0.10	<37
104	<0.10	12
105	<0.10	<4.7
108	<0.10	<32
109	<0.90	1.8
13	<0.030	0.16
118	0.0040	0.50
112	0.0060	0.24
13	<0.040	<0.066
117	0.0023	0.49

Source: Reference 47.

**TABLE 6-14. MERCURY EMISSION FACTORS FOR CRUDE OIL COMBUSTION  
GENERATED FROM CALIFORNIA "HOT SPOTS" TESTS**

Process type	Fuel oil type	Calculated mercury emission factor <sup>a</sup>						Measured mercury emission factor <sup>a</sup>					
		kg/10 <sup>15</sup> J	lb/10 <sup>12</sup> Btu	g/Mg fuel oil	10 <sup>-3</sup> lb/ton fuel oil	g/10 <sup>3</sup> L fuel oil	lb/10 <sup>6</sup> gal fuel oil	kg/10 <sup>15</sup> J	lb/10 <sup>12</sup> Btu	g/Mg fuel oil	10 <sup>-3</sup> lb/ton fuel oil	g/10 <sup>3</sup> L fuel oil	lb/10 <sup>6</sup> gal fuel oil
Pipeline/ process heater <sup>b</sup>	Crude	<2.4	<5.6	<0.10	<0.20	<0.097	<0.81	<0.052	<0.12	<0.0022	<0.0044	<0.0021	<0.018
Generator <sup>c</sup>	Crude	<2.4	<5.6	<0.10	<0.21	<0.10	<0.83	14.7	34.1	0.62	1.2	0.61	5.1

Source: Reference 54; Reference 57.

<sup>a</sup>Emission factors were based on assumed crude oil heating value of 42,500 kJ/kg (18,300 Btu/lb) and density of 0.97 kg/L (8.1 lb/gal).

<sup>b</sup>Mercury detection limit is 0.1 mg/kg.

<sup>c</sup>Mercury detection limit is 0.1 mg/L.

and heating value data, expands the range even further. Because these data are quite sparse and the relative quality of the data is uncertain, the midpoint of the range was selected as the best "typical" emission factor.

The uncontrolled emission factors for distillate, residual, and crude oil are presented in Table 6-15. Data are insufficient to develop controlled emission factors for fuel oil combustion. There is considerable uncertainty in these emission factor estimates due to the variability of mercury concentrations in fuel oil, the incomplete data base on distillate oil, and the uncertainty in sampling and analysis for detecting mercury. Therefore, these estimates should not be used to determine emissions from specific oil-fired units.

TABLE 6-15. BEST TYPICAL MERCURY EMISSION FACTORS FOR FUEL OIL COMBUSTION

Fuel oil type	Typical mercury emission factors					
	kg/10 <sup>15</sup> J	lb/10 <sup>12</sup> Btu	g/Mg fuel oil	10 <sup>-3</sup> lb/ton fuel oil	g/10 <sup>3</sup> L fuel oil	lb/10 <sup>6</sup> gal fuel oil
Residual No. 6	0.20	0.46	0.009	0.017	0.0085	0.071
Distillate No. 2	2.7	6.2	0.12	0.24	0.10	0.86
Crude	41	95	1.7	3.5	1.7	14

Total 1994 mercury emissions from oil combustion (utility, industrial, and commercial/residential) are estimated to be 7.6 Mg (8.4 tons); see Appendix A for details.

### 6.3 WOOD COMBUSTION

Wood and wood wastes are used as fuel in both the industrial and residential sectors. In the industrial sector, wood waste is fired in industrial boilers to provide process heat, while wood is burned in fireplaces and wood stoves in the residential sector. Studies have shown that wood and wood wastes may contain mercury; however, insufficient data are available to estimate the typical mercury content in wood and wood wastes. The information below includes process descriptions for the three combustion processes (boilers, fireplaces, and wood stoves), descriptions of the control measures used for wood-fired processes, and emission factors.

#### 6.3.1 Process Description

**6.3.1.1 Industrial Boilers.** Wood waste combustion in boilers is confined primarily to those industries in which wood waste is available as a byproduct. These boilers are used to generate heat energy and to alleviate potential solid waste disposal problems. In boilers, wood waste is normally burned in the form of hogged wood, bark, sawdust, shavings, chips, mill rejects, sanderdust, or wood trim. Heating values for this waste range from about 9,300 to 12,000 kJ/kg (4,000 to 5,000 Btu/lb) of fuel on a wet, as-fired basis. The moisture content of as-fired wood is typically near 50 weight percent, but may vary from 5 to 75 weight percent, depending on the waste type and storage operations. Generally, bark is the major type of waste burned in pulp mills; either a mixture of wood and bark waste or wood waste alone is burned most frequently in the lumber, furniture, and plywood industries.<sup>58</sup> One National Council of the Paper Industry for Air and Stream Improvement (NCASI) study found the mercury content of bark waste to range from <0.08 to 0.84 ppmwt.<sup>59</sup>

As of 1980, there were about 1,600 wood-fired boilers operating in the U.S., with a total capacity of approximately 30.5 gigawatts (GW) ( $1.04 \times 10^{11}$  Btu/hr).<sup>60</sup> No specific data on the distribution of these boilers were identified, but most are likely to be located where pulp and paper mills or other wood product plants are located (i.e., in the Southeast, Pacific Northwest, Wisconsin, Michigan, and Maine).

Various boiler firing configurations are used for burning wood waste. One common type of boiler used in smaller operations is the Dutch oven. This unit is widely used because it can burn fuels with very high moisture content. Fuel is fed into the oven through an opening in the top of a refractory-lined furnace. The fuel accumulates in a cone-shaped pile on a flat or sloping grate. Combustion is accomplished in two stages: (1) drying and gasification and (2) combustion of gaseous products. The first stage takes place in the primary furnace, which is separated from the secondary furnace chamber by a bridge wall. Combustion is

completed in the secondary chamber before gases enter the boiler section. The large mass of refractory helps to stabilize combustion rates but also causes a slow response to fluctuating steam demand.<sup>58</sup>

In another boiler type, the fuel cell oven, fuel is dropped onto suspended fixed grates and is fired in a pile. Unlike the Dutch oven, the refractory-lined fuel cell also uses combustion air preheating and positioning of secondary and tertiary air injection ports to improve boiler efficiency. Because of their overall design and operating similarities, however, fuel cell and Dutch oven boilers have comparable emission characteristics.<sup>58</sup>

The most common firing method employed for wood-fired boilers with a steam generation rate greater than 45,000 kg/hr (100,000 lb/hr) is the spreader stoker. With this boiler, wood enters the furnace through a fuel chute and is spread either pneumatically or mechanically across the furnace, where small pieces of the fuel burn while in suspension. Simultaneously, larger pieces of fuel are spread in a thin, even bed on a stationary or moving grate. The burning is accomplished in three stages in a single chamber: (1) moisture evaporation; (2) distillation and burning of volatile matter; and (3) burning of fixed carbon. This type of boiler has a fast response to load changes, has improved combustion control, and can be operated with multiple fuels. Natural gas, oil, and/or coal, are often fired in spreader stoker boilers as auxiliary fuels. The fossil fuels are fired to maintain a constant steam supply when the wood waste moisture content or mass rate fluctuates and/or to provide more steam than can be generated from the wood waste supply alone. Although spreader stokers are the most common stokers among larger wood-fired boilers, overfeed and underfeed stokers are also utilized for smaller units.<sup>58</sup>

Another boiler type sometimes used for wood combustion is the suspension-fired boiler. This boiler differs from a spreader stoker in that small-sized fuel (normally less than 2 mm [0.08 in.]) is blown into the boiler and combusted by supporting it in air rather than on fixed grates. Rapid changes in combustion rate and, therefore, steam generation rate are possible because the finely divided fuel particles burn quickly.<sup>58</sup>

A recent innovation in wood firing is the fluidized bed combustion (FBC) boiler. A fluidized bed consists of inert particles through which air is blown so that the bed behaves as a fluid. Wood waste enters in the space above the bed and burns both in suspension and in the bed. Because of the large thermal mass represented by the hot inert bed particles, fluidized beds can handle fuels with moisture contents up to near 70 percent (wet basis). Fluidized beds also can handle dirty fuels (up to 30 percent inert material). Wood fuel is pyrolyzed faster in a fluidized bed than on a grate due to its immediate contact with hot bed material. As a result, combustion is rapid and results in nearly complete combustion of the organic matter, thereby minimizing emissions of unburned organic compounds.<sup>58</sup>

**6.3.1.1 Residential Wood Stoves.** Wood stoves are enclosed wood heaters that control burning or burn time by restricting the amount of air that can be used for combustion. They are commonly used in residences as space heaters, both as the primary source of residential heat and as a supplement to conventional heating systems. Based on known variations in construction, combustion, and emission characteristics, there are five different categories of residential wood burning devices: (1) the conventional wood stove; (2) the noncatalytic wood stove; (3) the catalytic wood stove; (4) the pellet stove; and (5) the masonry heater.<sup>61</sup>

The conventional stove category comprises all stoves without catalytic combustors not included in the other noncatalytic categories (i.e., noncatalytic and pellet). Conventional stoves do not have any emissions reduction technology or design features and, in most cases, were manufactured before July 1, 1986. Stoves of many different airflow designs may be in this category, such as updraft, downdraft, crossdraft, and S-flow.<sup>61</sup>

Noncatalytic wood stoves are those units that do not employ catalysts but do have emission-reducing technology or features. Typical noncatalytic design includes baffles and secondary combustion chambers.<sup>61</sup>

Catalytic stoves are equipped with a ceramic or metal honeycomb device, called a combustor or converter, that is coated with a noble metal such as platinum or palladium. The catalyst material reduces the ignition temperature of the unburned volatile organic compounds (VOC's) and carbon monoxide (CO) in the exhaust gases, thus augmenting their ignition and combustion at normal stove operating temperatures. As these components of the gases burn, the temperature inside the catalyst increases to a point at which the ignition of the gases is essentially self-sustaining.<sup>61</sup>

Pellet stoves are those fueled with pellets of sawdust, wood products, and other biomass materials pressed into manageable shapes and sizes. These stoves have active air flow systems and unique grate design to accommodate this type of fuel.<sup>61</sup>

Masonry heaters are large, enclosed chambers made of masonry products or a combination of masonry products and ceramic materials. Masonry heaters are gaining popularity as a cleaner-burning, heat-efficient form of primary and supplemental heat, relative to some other types of wood heaters. In a masonry heater, a complete charge of wood is burned in a relatively short period of time. The use of masonry materials promotes heat transfer. Thus, radiant heat from the heater warms the surrounding area for many hours after the fire has burned out.<sup>61</sup>

**6.3.1.2 Residential Fireplaces.** Fireplaces are used primarily for aesthetic effects and secondarily as a supplemental heating source in homes and other dwellings. Wood is most commonly used as fuel, but coal and densified wood "logs" also may be burned. The user intermittently adds fuel to the fire by hand.<sup>62</sup>

Fireplaces can be divided into two broad categories: (1) masonry (generally brick and/or stone, assembled on site, and integral to a structure) and (2) prefabricated (usually metal, installed on site as a package with appropriate duct work).<sup>62</sup>

Masonry fireplaces typically have large fixed openings to the fire bed and have dampers above the combustion area in the chimney to limit room air and heat losses when the fireplace is not being used. Some masonry fireplaces are designed or retrofitted with doors and louvers to reduce the intake of combustion air during use.<sup>62</sup>

Prefabricated fireplaces are commonly equipped with louvers and glass doors to reduce the intake of combustion air, and some are surrounded by ducts through which floor level air is drawn by natural convection, heated, and returned to the room.<sup>62</sup>

All of the systems described above operate at temperatures that are above the boiling point of mercury and mercury compounds. Consequently, any mercury contained in the wood fuel will be emitted with the combustion gases via the exhaust stack.

### **6.3.2 Emission Control Measures**

Although some wood stoves use emission control measures such as catalysts and secondary combustion chambers to reduce VOC and CO emissions, these techniques are not expected to affect mercury emissions. However, wood-fired boilers employ PM control equipment which may provide some reduction. These systems are described briefly below.

Currently, the four most common control devices used to reduce PM emissions from wood-fired boilers are mechanical collectors, fabric filters, wet scrubbers, and electrostatic precipitators (ESP's).<sup>58</sup> Of these controls, only the last two have the potential for significant mercury reduction.

The most widely used wet scrubbers for wood-fired boilers are venturi scrubbers. With gas-side pressure drops exceeding 4 kilopascals (kPa) (15 inches of water), PM collection efficiencies of 90 percent or greater have been reported for venturi scrubbers operating on wood-fired boilers.<sup>58</sup> No data were located on the performance of these systems relative to mercury emissions. However, some control is expected (probably in the range of 50 to 90 percent) based on results achieved for coal combustion sources.

Fabric filters (i.e., baghouses) and ESP's are employed when PM collection efficiencies above 95 percent are required. Collection efficiencies of 93 to 99.8 percent for PM have been observed for ESP's operating on wood-fired boilers, but mercury efficiencies are likely to be substantially lower (probably 50 percent or less) based on the performance of ESP's in controlling mercury from coal combustion sources.<sup>58</sup> The performance of ESP's in controlling mercury emissions depends on operating temperature and the amount of carbon in the fly ash.

Fabric filters have had limited applications to wood-fired boilers. The principal drawback to fabric filtration, as perceived by potential users, is a fire danger arising from the collection of combustible carbonaceous fly ash. Despite potential complications, fabric filters are generally preferred for boilers firing salt-laden wood. This fuel produces fine PM with a high salt content for which fabric filters can achieve high collection efficiencies. In two tests of fabric filters operating on salt-laden wood-fired boilers, PM collection



efficiencies were above 98 percent.<sup>58</sup> No data are available on mercury emission reduction for fabric filters, but results for other combustion sources suggest that efficiencies will be very low.

### 6.3.3 Emissions

The primary source of mercury emissions from wood combustion processes is the combustion gas exhaust stack. Very small quantities of mercury also may be emitted with the fugitive PM emissions from bottom and fly ash handling operations.

The data on mercury emissions from wood combustion are limited. A recent National Council of the Paper Industry for Air and Stream Improvement (NCASI) report provided a range and average emission factor for boilers without electrostatic precipitators (ESP's) and for boilers with ESP's.<sup>63</sup> The boilers without ESP's included a variety of control devices including cyclones, multiclones, and various wet scrubbers. The average emission factor reported for boilers without ESP's was  $3.5 \times 10^{-6}$  kg/Mg ( $6.9 \times 10^{-6}$  lb/ton) of dry wood burned. The average emission factor reported for boilers with ESP's was  $1.3 \times 10^{-6}$  kg/Mg ( $2.6 \times 10^{-6}$  lb/ton) of dry wood burned.

The most recent AP-42 section on wood waste combustion in boilers provided an average uncontrolled emission factor for mercury emissions based on four emission test reports.<sup>58</sup> The AP-42 uncontrolled emission factor for mercury emissions from wood waste combustion is  $2.6 \times 10^{-6}$  kg/Mg ( $5.2 \times 10^{-6}$  lb/ton) of wet, as-fired wood burned.

The NCASI average emission factor reported for wood-fired boilers with ESP's of  $1.3 \times 10^{-6}$  kg/Mg ( $2.6 \times 10^{-6}$  lb/ton) of dry wood burned is recommended for estimating mercury emissions from wood waste combustion in boilers.

For residential wood combustion, only one emission factor was found in the literature.<sup>64</sup> This emission factor is based on one test burning one type of wood (pine) at a single location. In 1987, the Department of Energy estimated that 22.5 million households burned approximately 42.6 million cords of wood.<sup>65</sup> Given that the density of wood varies greatly by wood species and moisture content, and that the above emission factor is from a single test, nationwide emissions of mercury from residential wood combustion were not estimated.

Total 1994 mercury emissions from wood combustion are estimated to be 0.1 Mg (0.1 tons); see Appendix A for details.

## 6.4 MUNICIPAL WASTE COMBUSTION

Refuse or municipal solid waste (MSW) consists primarily of household garbage and other nonhazardous commercial, institutional, and nonmanufacturing industrial solid waste. Municipal waste combustors (MWC's) are used to reduce the mass and volume of MSW that ultimately must be landfilled. In fact, MWC's reduce the volume of MSW by about 90 percent.

In the previous mercury L&E, it was estimated that there were over 160 MWC plants in operation in the United States with capacities greater than 36 megagrams per day (Mg/d) [40 tons per day (ton/d)] and a total capacity of approximately 100,000 Mg/d (110,000 ton/d) of MSW.<sup>32</sup> A number of MWC plants have closed since 1991. At the beginning of 1995, over 130 MWC plants with aggregate capacities of greater than 36 Mg/d (40 ton/d) of MSW were operating in the United States. The number of combustion units per facility ranges from one to six, with the average being two. Total facility capacity ranges from 36 to 2,700 Mg/d (40 to 3,000 ton/d). Together these plants have a total capacity of approximately 90,000 Mg/d (99,000 ton/d).<sup>66</sup>

In addition to the MWC's discussed above, a number of smaller MWC's in the United States have plant capacities of less than 36 Mg/d (40 ton/d). This population of smaller MWC's comprises a very small fraction of the nation's total MWC capacity.

Table 6-16 shows the geographic distribution of MWC units and capacities by States for MWC plants larger than 35 Mg/d. This distribution reflects the MWC's that were operational in 1995.<sup>67</sup>

#### 6.4.1 Municipal Solid Waste Characteristics

Municipal solid waste is a heterogeneous mixture of the various materials found in household, commercial, institutional, and nonmanufacturing industrial wastes. Major constituents in typical municipal waste are listed in Table 6-17. In 1994, a total of 145.24 million Mg (159.76 million tons) of municipal solid waste was discarded in the municipal waste stream. Of this total, 74.8 percent was due to materials in discarded products and 25.2 percent other waste, such as food wastes and yard trimmings.<sup>68</sup> Known sources of mercury in MSW are batteries, discarded electrical equipment and wiring, fluorescent bulbs, paint residues, and plastics. As of 1989, 644 Mg (709 tons) of mercury were reported to be discarded in the municipal solid waste stream, and the concentration of mercury in solid waste is reported to be in the range of less than 1 to 6 ppm by weight with a typical value of 4 ppm by weight. However, because of changes in mercury consumption, the quantity of mercury discarded in the municipal solid waste stream has decreased dramatically since 1989 and is expected to decrease in the future.<sup>69,70</sup>

The most recent report on mercury discarded in solid municipal waste was a 1992 EPA report based on 1989 data with projections to the year 2000. One of the most common sources of mercury in this waste was from the discard of batteries; in 1989, it was estimated that about 88 percent of the total discard of mercury was from batteries. Of the 88 percent, about 28 percent was from mercuric oxide batteries and the remainder from alkaline and other batteries.<sup>38</sup> According to the Bureau of Mines (now part of USGS) estimates, 250 Mg (275 tons) of mercury were used in battery production in 1989; current USGS estimates for 1995 are 6 Mg (6.6 tons) and for 1996, less than 0.5 Mg (0.55 tons).<sup>2</sup> As discussed in Section 5.2, only mercuric oxide button cells and the larger mercuric oxide batteries use mercury to any extent. The proportion of mercury usage between the button cells and the larger batteries is not available but essentially all of the larger batteries are used in hospital and military applications and, therefore, would generally not be contained in the municipal solid waste stream. Battery discards from hospital and military applications would be either recycled or disposed at the facility.<sup>30,71</sup> Hospital battery discards incinerated at the facility would be a component of the medical waste combustion estimates.

#### 6.4.2 Process Description

The three principal MWC classes are mass burn, refuse-derived fuel (RDF), and modular combustors. The paragraphs below briefly describe some of the key design and operating characteristics of these different combustor types.<sup>72,73</sup>

In mass burn units, the MSW is combusted without any preprocessing other than removal of items too large to go through the feed system. In a typical mass burn combustor, unprocessed waste (after removal of bulky, noncombustible items) is delivered by an overhead crane to a feed hopper. From the feed hopper, refuse is fed into the combustion chamber on a moving grate. Combustion air in excess of stoichiometric amounts is supplied below (underfire air) and above (overfire air) the grate. Mass burn combustors are usually erected at the site (as opposed to being prefabricated at another location) and range in size from 46 to 900 Mg/day (50 to 1,000 tons/d) of MSW throughput per unit. The mass burn combustor category can be divided into mass burn refractory wall (MB/REF), mass burn/waterwall (MB/WW), and mass burn/rotary waterwall (MB/RC) designs. The two most common, MB/WW and MB/REF, are described below.

The MB/WW design represents the predominant technology in the existing population of large MWC's, and it is expected that the majority of new units will be MB/WW designs. In MB/WW units, the combustor walls are constructed of metal tubes that contain pressurized water and recover radiant energy from the combustion chamber. Trucks deliver MSW to a large pit, where the waste is mixed and bulky items are removed. After removal of large, bulky items and noncombustibles, unprocessed waste is delivered by an overhead crane to a feed hopper that conveys the waste into the combustion chamber. Nearly all modern MB/WW facilities utilize reciprocating grates or roller grates to move the waste through the combustion chamber. The grates typically include two or three separate sections where designated

TABLE 6-16. SUMMARY OF GEOGRAPHICAL DISTRIBUTION  
OF MWC FACILITIES LARGER THAN 35 Mg/d

State	No. of MWC facilities	State MWC capacity Mg/d (ton/d)	Percentage of total MWC capacity in the United States
AK	2	109 (120)	<0.5
AL	1	627 (690)	0.67
AR	4	257 (283)	0.28
CA	3	2,324 (2,560)	2.5
CT	6	5,489 (6,045)	5.9
FL	13	15,480 (17,048)	17
GA	1	454 (500)	0.49
HI	1	1,961 (2,160)	2.1
ID	1	45 (50)	0.05
IL	1	1,453 (1,600)	1.6
IN	1	2,145 (2,362)	2.3
MA	9	9,770 (10,760)	11
MD	4	4,821 (5,310)	5.2
ME	4	1,816 (2,000)	2.0
MI	5	4,744 (5,225)	5.1
MN	12	4,633 (5,102)	5.0
MS	1	136 (150)	<0.5
MT	1	65 (72)	<0.5
NC	3	657 (724)	0.71
NH	3	755 (832)	0.81
NJ	6	5,286 (5,822)	5.7
NY	12	9,584 (10,555)	10
OH	2	545 (600)	0.59
OK	2	1,117 (1,230)	1.2
OR	2	613 (675)	0.66
PA	7	7,901 (8,702)	8.5
SC	2	790 (870)	0.85
TN	2	1,135 (1,250)	1.2
TX	3	177 (195)	0.19
UT	1	363 (400)	0.39
VA	6	5,743 (6,325)	6.2
WA	4	1,251 (1,378)	1.4
WI	4	755 (831)	0.81
Total	129 <sup>a</sup>	93,000 (102,400)	100

<sup>a</sup>There are a total of 129 MWC facilities which operate approximately 305 units.

Source: Reference 67.

TABLE 6-17. COMPOSITION OF DISPOSED  
RESIDENTIAL AND COMMERCIAL  
WASTE (WEIGHT PERCENT)

Component	Year, 1994
Paper and Paperboard	32.9
Yard Wastes	14.8
Food Wastes	8.5
Glass	6.4
Metals	6.3
Plastics	11.8
Wood	8.2
Textiles	3.6
Rubber and Leather	3.7
<u>Miscellaneous</u>	<u>3.8</u>
Totals	100.0

Source: Reference 68.

stages in the combustion process occur. On the initial grate section, referred to as the drying grate, the moisture content of the waste is reduced prior to ignition. In the second grate section, the burning grate, the majority of active burning takes place. The third grate section, referred to as the burnout or finishing grate, is where remaining combustibles in the waste are burned. Bottom ash is discharged from the finishing grate into a water-filled ash quench pit or ram discharger. From there, the moist ash is discharged to a conveyor system and transported to an ash loading area or storage area prior to disposal. Because the waste bed is exposed to fairly uniform high combustion temperatures, mercury and mercury compounds will be exhausted as vapors with the combustion gases.

The MB/REF combustors are older facilities that comprise several designs. This type of combustor is continuously fed and operates in an excess air mode with both underfire and overfire air provided. The waste is moved on a traveling grate and is not mixed as it advances through the combustor. As a result, waste burnout or complete combustion is inhibited by fuel bed thickness, and there is considerable potential for unburned waste to be discharged into the bottom ash pit. Rocking and reciprocating grate systems mix and aerate the waste bed as it advances through the combustion chamber, thereby improving contact between the waste and combustion air and increasing the burnout of combustibles. The system generally discharges the ash at the end of the grates to a water quench pit for collection and disposal in a landfill. The MB/REF combustors have a refractory-lined combustion chamber and operate at relatively high excess air rates to prevent excessive temperatures, which can result in refractory damage, slagging, fouling, and corrosion problems.

Because of their operating characteristics, the tracking grate systems may have cool ash pockets in which mercury and mercury compounds are not exposed to high temperature and are thereby retained in the ash, rather than being exhausted with the combustion gas stream. Consequently, mercury and mercury compounds may be emitted as fugitive emissions from ash handling. However, the combustion stack is the primary source of mercury emissions. In the rocking and reciprocating grate systems, essentially all mercury will be exhausted with the combustion gas.

Refuse-derived fuel combustors burn MSW that has been processed to varying degrees, from simple removal of bulky and noncombustible items accompanied by shredding, to extensive processing to produce a finely divided fuel suitable for co-firing in pulverized coal-fired boilers. Processing MSW to RDF generally raises the heating value of the waste because many of the noncombustible items are removed.

A set of standards for classifying RDF types has been established by the American Society for Testing and Materials (ASTM). The type of RDF used is dependent on the boiler design. Boilers that are

designed to burn RDF as the primary fuel usually utilize spreader stokers and fire fluff RDF in a semi-suspension mode. This mode of feeding is accomplished by using an air swept distributor, which allows a portion of the feed to burn in suspension and the remainder to be burned out after falling on a horizontal traveling grate. The number of RDF distributors in a single unit varies directly with unit capacity. The distributors are normally adjustable so that the trajectory of the waste feed can be varied. Because the traveling grate moves from the rear to the front of the furnace, distributor settings are adjusted so that most of the waste lands on the rear two-thirds of the grate to allow more time for combustion to be completed on the grate. Bottom ash drops into a water-filled quench chamber. Underfire air is normally preheated and introduced beneath the grate by a single plenum. Overfire air is injected through rows of high pressure nozzles, providing a zone for mixing and completion of the combustion process. Because essentially all of the waste is exposed to high combustion temperatures on the grate, most of the mercury in the RDF will be discharged with the combustion gas exhaust.

In a fluidized-bed combustor (FBC), fluff or pelletized RDF is combusted in a turbulent bed of noncombustible material, such as limestone, sand, or silica. In its simplest form, the FBC consists of a combustor vessel equipped with a gas distribution plate and an underfire air windbox at the bottom. The combustion bed overlies the gas distribution plate. The RDF may be injected into or above the bed through ports in the combustor wall. The combustor bed is suspended or "fluidized" through the introduction of underfire air at a high pressure and flow rate. Overfire air is used to complete the combustion process.

Good mixing is inherent in the FBC design. Fluidized-bed combustors have uniform gas temperatures and mass compositions in both the bed and in the upper region of the combustor. This uniformity allows the FBC's to operate at lower excess air and temperature levels than conventional combustion systems. Waste-fired FBC's typically operate at excess air levels between 30 and 100 percent and at bed temperatures around 815°C (1500°F). At this temperature, most mercury and mercury compounds will be volatilized and exhausted with the combustion gas stream as a vapor.

In terms of number of facilities, modular starved-(or controlled-) air (MOD/SA) combustors represent a notable segment of the existing MWC population. However, because of their small sizes, they account for only a small percentage of the total capacity. The basic design of a MOD/SA combustor consists of two separate combustion chambers, referred to as the "primary" and "secondary" chambers. Waste is batch-fed intermittently to the primary chamber by a hydraulically activated ram. The charging bin is filled by a front-end loader or by other mechanical systems. Waste is fed automatically on a set frequency, with generally 6 to 10 minutes between charges.

Waste is moved through the primary combustion chamber by either hydraulic transfer rams or reciprocating grates. Combustors using transfer rams have individual hearths upon which combustion takes place. Grate systems generally include two separate grate sections. In either case, waste retention times in the primary chamber are lengthy, lasting up to 12 hours. Bottom ash is usually discharged to a wet quench pit.

The quantity of air introduced in the primary chamber defines the rate at which waste burns. Combustion air is introduced in the primary chamber at substoichiometric levels, resulting in a flue gas rich in unburned hydrocarbons. The combustion air flow rate to the primary chamber is controlled to maintain an exhaust gas temperature set point [generally 650° to 980°C (1200° to 1800°F)], which corresponds to about 40 to 60 percent theoretical air. As the hot, fuel-rich flue gases flow to the secondary chamber, they are mixed with excess air to complete the burning process. Because the temperature of the exhaust gases from the primary chamber is above the autoignition point, completing combustion is simply a matter of introducing air to the fuel-rich gases. The amount of air added to the secondary chamber is controlled to maintain a desired flue gas exit temperature, typically 980° to 1200° (1800° to 2200°F). At these primary chamber and secondary chamber temperatures, essentially all of the mercury contained in the waste is expected to be emitted as a vapor from the secondary chamber with the combustion gas stream.

#### 6.4.3 Emission Control Measures

Mercury emissions from MWC units are controlled to a limited extent by adsorbing the mercury vapors from the combustion chamber onto the acid gas sorbent material and then removing the particle-phase mercury with a high-efficiency PM control device. The PM control devices most frequently used in the United States are ESP's and fabric filters. To achieve this mercury control, reducing flue gas temperature at the inlet to the control device to 175°C (350°F) or less is beneficial.<sup>74</sup> Typically, newer MWC systems use a

combination of gas cooling and duct sorbent injection (DSI) or spray dryer (SD) systems upstream of the PM device to reduce temperatures and provide a mechanism for acid gas control.

The information contained in Reference 74 suggests that these combined acid gas/PM systems can achieve improved mercury control by injecting activated carbon or modified activated carbon into the flue gas upstream from the DSI or SD unit. With activated carbon injection, mercury control is increased to 90 percent. The paragraphs below briefly describe the DSI and SD processes. Because the ESP's and FF's used on MWC's are comparable to those used on other combustion systems, they are not described.

Spray drying in combination with either fabric filtration or an ESP is the most frequently used acid gas control technology for MWC's in the United States. Spray dryer/fabric filter systems are more common than SD/ESP systems and are used most on new, large MWC's. In the spray drying process, lime is slurried and then injected into the SD through either rotary atomizer or dual-fluid nozzles. The key design and operating parameters that significantly affect SD acid gas performance are the SD's outlet temperature and lime-to-acid gas stoichiometric ratio. The SD outlet temperature, which affects mercury removal, is controlled by the amount of water in the lime slurry.<sup>72</sup>

With DSI, powdered sorbent is pneumatically injected into either a separate reaction vessel or a section of flue gas duct located downstream of the combustor economizer. Alkali in the sorbent (generally calcium) reacts with HCl and SO<sub>2</sub> to form alkali salts (e.g., calcium chloride [CaCl<sub>2</sub>] and calcium sulfite [CaSO<sub>3</sub>]). Some units also use humidification or other temperature control measures upstream from the collection device. Reaction products, fly ash, and unreacted sorbent are collected with either an ESP or fabric filter.<sup>72</sup>

Recent test programs using activated carbon injection have been conducted in the United States. Recent test results have shown mercury removal efficiencies from 90 percent to over 95 percent with activated carbon injection.<sup>67</sup> Other test results show mercury reductions ranging from 50 to over 95 percent, depending on the carbon feed rate, with typical outlet Hg concentrations of less than 50 µg/dscm.<sup>67,72,74</sup> As a result of the emission standards developed for municipal waste combustors under section 129 of the Clean Air Act Amendments, new (subpart Eb) and existing (subpart Cb), MWC's will typically operate with spray dryer/fabric filter systems with activated carbon injection.

#### 6.4.4 Emissions

The primary source of mercury emissions from municipal waste combustors is the combustion gas exhaust stack. However, small amounts of mercury may be emitted as part of the fugitive PM emissions from fly ash handling, particularly if highly efficient dry control systems are used.

A recent EPA report documenting 1995 estimates of the mercury emissions from municipal waste combustors indicates that mercury emissions from MWC's decreased by 48 percent between 1990 and 1995.<sup>67</sup> Estimated 1990 mercury emissions were 49 Mg (54 tons) and for 1995, emissions are estimated to be 26 Mg (29 tons). This decrease in mercury emissions is attributed to retrofits of air pollution controls on some MWC's, retirement of several existing MWC's, and significant reductions in uncontrolled mercury emissions due to decreased levels of mercury in consumer products such as batteries. The inventory of MWC's used to develop the 1995 estimates of mercury emissions is presented in Appendix B. Relative to the 1990 nationwide emissions of mercury from MWC's, a 92 percent reduction in mercury levels (to 4.0 Mg or 4.4 tons) is projected by about 2000 as a result of the section 129 emission standards (subpart Eb) and guidelines (subpart Cb) for MWC's.<sup>67</sup>

A recent study conducted to update the municipal waste combustor section of AP-42 provided a comprehensive review of the available MWC mercury emission data. The study found that most of the test reports contained insufficient process data to generate emission factors. The authors of the municipal waste combustion section of AP-42 concluded that the development of emission factors for MWC's, using only the test reports which estimated feed rates, would eliminate data from so many facilities that the values derived were not likely to be representative of the entire MWC population. In addition, the subjective nature of the refuse feed rates called into question the validity of the limited data. Consequently, emission factors were developed using the F-factor, which is the ratio of the gas volume of the products of combustion (e.g., flue gas volume) to the heating value of the fuel. This approach, presented in EPA Method 19, requires an F-factor and an estimate of the fuel heating value. For MWC's, the F-factor is 0.257 dscm/MJ (9,570 dscf/10<sup>6</sup> Btu) (at 0 percent O<sub>2</sub>) of MSW fired. For all combustor types, except RDF combustors, a heating value of 10,500 kJ/kg (4,500 Btu/lb) refuse was assumed. For RDF combustor units, the processed refuse

has a higher heating value, and a heating value of 12,800 kJ/kg (5,500 Btu/lb) was assumed. Overall, these data are representative of average values for MWC's.<sup>72</sup> While this procedure does provide good average emission factors that represent an industry cross section, the assumed F-factor and waste heating values above may not be appropriate for specific facilities.

As mentioned earlier, the concentration of mercury in consumer products has declined since 1989. As a result, the concentration of mercury in municipal solid has declined. The same methodology used to develop the AP-42 emission factors was applied to the average mercury concentrations presented in Reference 67. These average mercury concentrations and the resultant average emission factors are presented in Table 6-18. While the procedure used to develop the emission factors presented in Table 6-18 does provide good average emission factors that represent the industry cross section, the assumed F-factors and waste heating values above may not be appropriate for specific facilities.

TABLE 6-18. AVERAGE EMISSION FACTORS FOR MUNICIPAL WASTE COMBUSTORS

Combustor type	Mercury concentration ug/dscm @ 7% O <sub>2</sub>	Average emission factors	
		g/Mg waste	10 <sup>-3</sup> lb/ton waste
Non-RDF without AG control	340	1.4	2.8
Non-RDF with AG control	205	0.83	1.7
Non-RDF with AG control and carbon	19	0.077	0.15
RDF without AG control	260	1.3	2.6
RDF with AG control	35	0.17	0.34

AG = acid gas control (includes SD, DSI/FF, SD/ESP, DSI/ESP, SD/FF, and SD/ESP configurations)

Non-RDF = Combustors that burn MSW (e.g, MB/WW, MB/RW, MOD/EA, MOD/SA)

RDF = Combustors that burn refused derived fuel

Total 1995 mercury emissions from municipal waste combustion are estimated to be 26 Mg (29 tons); see Appendix A for details.

## 6.5 SEWAGE SLUDGE INCINERATORS

Currently, there are 166 active sewage sludge incinerators (SSI's) in the United States using one of three technologies: multiple hearth, fluidized-bed, and electric infrared. Over 80 percent of the identified, operating SSI's are multiple hearth units. About 15 percent of the SSI's are fluidized-bed combustors; 3 percent are electric infrared; and the remainder cofire sewage sludge with municipal solid waste.<sup>75</sup>

Most sewage sludge incineration facilities are located in the eastern United States, but a substantial number are also located on the West Coast. New York has the largest number of SSI facilities with 33, followed by Pennsylvania and Michigan with 21 and 19, respectively. About 785,000 Mg (865,000 tons) of sewage sludge on a dry basis are estimated to be incinerated annually.<sup>76</sup>

The most recent data on the mercury content of sewage sludge obtained from the 1988 National Sewage Sludge Survey show a mean mercury concentration of 5.2 ppmwt (parts per million by weight).<sup>77</sup> Earlier data obtained in the mid 1970's indicate that mercury concentrations in municipal sewage sludge range from 0.1 to 89 ppmwt with a mean value of 7 ppmwt and a median value of 4 ppmwt.<sup>9</sup> Other early data collected by EPA from 42 municipal sewage treatment plants in the early 1970's showed a range of 0.6 to 43 ppmwt, with a mean value of 4.9 ppmwt on a dry solids basis.<sup>78</sup> The potential for the formation of volatile organomercury compounds during the waste treatment process was considered. According to two sources, no test data are available for emissions of organomercury compounds from this source.<sup>79,80</sup> These sources expect any level of formation would be very low.

The sections below provide SSI process descriptions, a discussion of control measures, and a summary of mercury emission factors.

### 6.5.1 Process Description

Figure 6-1 presents a simplified diagram of the sewage sludge incineration process, which involves two primary steps. The first step in the process of sewage sludge incineration is the dewatering of the sludge. Sludge is generally dewatered until it is about 20 to 35 percent solids. Systems using Thermal Conditioning Processes regularly obtain dewatered sludge that contains in excess of 40 percent solids. When it is more than 25 percent solids, the sludge will usually burn without auxiliary fuel. After dewatering, the sludge is sent to the incinerator, and thermal oxidation occurs. The unburned residual ash is removed from the incinerator, usually on a continuous basis, and is disposed in a landfill or reused (i.e., bricks, concrete, asphalt, etc.). A portion of the noncombustible waste, as well as unburned volatile organic compounds, is carried out of the combustor through entrainment in the exhaust gas stream. Air pollution control devices, primarily wet scrubbers, are used to remove the entrained pollutants from the exhaust gas stream. The gas stream is then exhausted, and the collected pollutants are sent back to the head of the wastewater treatment plant in the scrubber effluent. As shown in Figure 6-1, the primary source of mercury emissions from the SSI process is the combustion stack. Some fugitive emissions may be generated from ash handling, but the quantities are expected to be small. Because mercury and mercury compounds are relatively volatile, most mercury will leave the combustion chamber in the exhaust gas; concentrations in the ash residue are expected to be negligible.

The paragraphs below briefly describe the three primary SSI processes used in the United States.<sup>75</sup>

The basic multiple hearth furnace is cylindrical in shape and is oriented vertically. The outer shell is constructed of steel, lined with refractory, and surrounds a series of horizontal refractory hearths. A hollow cast iron rotating shaft runs through the center of the hearths. Attached to the central shaft are the rabble arms with teeth shaped to rake the sludge in a spiral motion, alternating in direction from the outside in, then inside out, between hearths. Typically, the upper and lower hearths are fitted with four rabble arms, and the middle hearths are fitted with two. Cooling air for the center shaft and rabble arms is introduced into the shaft by a fan located at its base. Burners that provide auxiliary heat are located in the sidewalls of the hearths.

In the majority of multiple hearth incinerators, dewatered sludge is fed directly onto the top hearth. For a number of incinerators, the sludge is fed directly to a lower hearth. Typically, the rabble arms move the sludge through the incinerator as the motion of the rabble arms rakes the sludge toward the center shaft, where it drops through holes located at the center of the hearth. This process is repeated in all of the subsequent hearths, with the sludge moving in opposite directions in adjacent hearths. The effect of the rabble motion is to break up solid material to allow better surface contact with heat and oxygen.

Ambient air is first ducted through the central shaft and its associated rabble arms. The center shaft cooling air exhaust is either sent back to a lower hearth or it is piped to the incinerator's exhaust stack for "plume suppression". The combustion air flows upward through the drop holes in the hearths, countercurrent to the flow of the sludge, before being exhausted from the top hearth.

Multiple hearth furnaces can be divided into three zones. The upper hearths comprise the drying zone where most of the moisture in the sludge is evaporated. The temperature in the drying zone is typically between 425° and 760°C (800° and 1400°F). Sludge combustion occurs in the middle hearths (second zone) as the temperature is increased to a maximum of 925°C (1700°F). When exposed to the temperatures in both upper zones, most mercury will be volatilized and discharged as vapor in the exhaust gas. The third zone, made up of the lowermost hearth(s), is the cooling zone. In this zone, the ash is cooled as its heat is transferred to the incoming combustion air.

Fluidized-bed combustors (FBC's) are cylindrically shaped and vertically oriented. The outer shell is constructed of steel and lined with refractory. Tuyeres (nozzles designed to deliver blasts of air) are located at the base of the furnace within a refractory-lined grid. A bed of sand rests upon the grid. Dewatered sludge is fed into the bed of the furnace. Air injected through the tuyeres, at pressures from



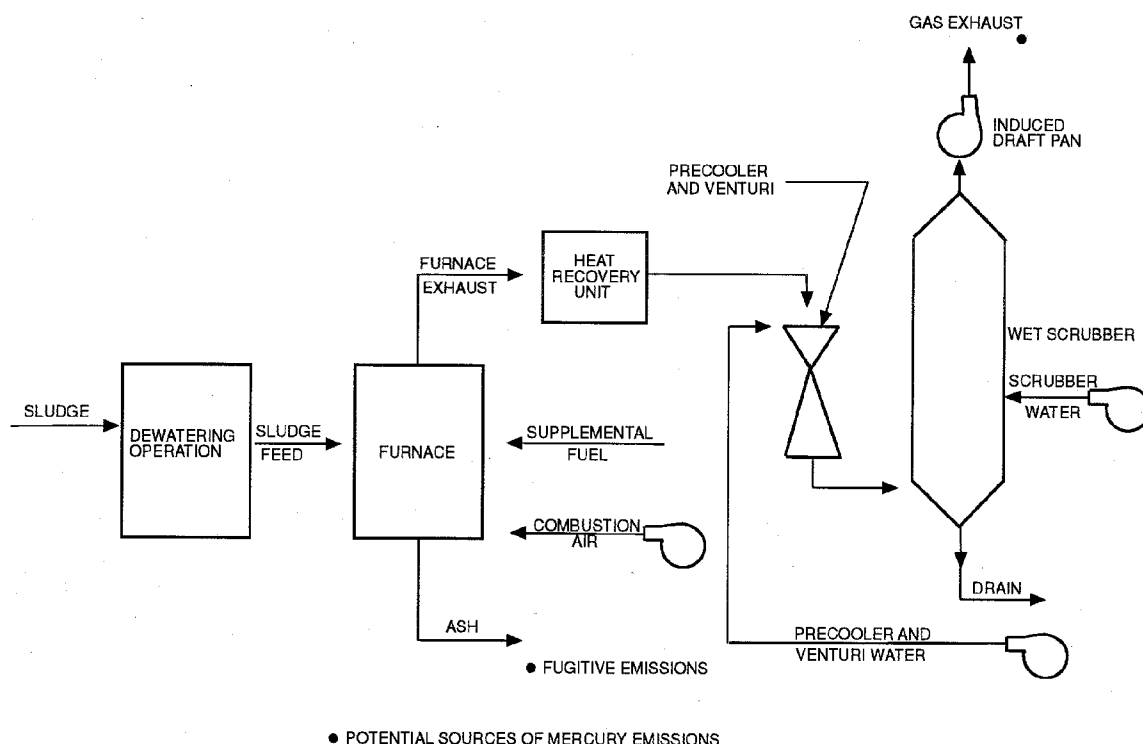


Figure 6-1. Process flow diagram for sludge incineration.

20 to 35 kPa (3 to 5 psig), simultaneously fluidizes the bed of hot sand and the incoming sludge. Normally a temperature of 677° (1250°F), which is sufficient to vaporize most mercury contained in the sludge, is maintained in the bed. As the sludge burns, fine ash particles and mercury vapor are carried out the top of the furnace with the exhaust gas.

An electric infrared incinerator consists of a horizontally oriented, insulated furnace. A woven wire belt conveyor extends the length of the furnace, and infrared heating elements are located in the roof above the conveyor belt. Combustion air is preheated by the flue gases and injected into the discharge end of the furnace. Electric infrared incinerators consist of a number of prefabricated modules that are linked together to provide the required furnace length. The dewatered sludge cake is conveyed into one end of the incinerator. An internal roller mechanism levels the sludge into a continuous layer approximately 2.5 centimeters (cm) [1 inch (in.)] thick across the width of the belt. The sludge is sequentially dried and then burned as it moves beneath the infrared heating elements. Ash is discharged into a hopper at the opposite end of the furnace. The preheated combustion air enters the furnace above the ash hopper and is further heated by the outgoing ash. The direction of air flow is countercurrent to the movement of the sludge along the conveyor.

In addition to the three technologies discussed above, other technologies have been used for incineration of sewage sludge. Three of these processes are cyclonic reactors, rotary kilns, and wet oxidation reactors; none of these processes find widespread usage in the United States.

### 6.5.2 Emission Control Measures

Most SSI's are equipped with some type of wet scrubbing system for PM control. Because these systems provide gas cooling as well as PM removal, they can potentially provide some mercury control. Limited data obtained on mercury removal efficiencies are presented in the emission factor discussion. The paragraphs below briefly describe the wet scrubbing systems typically used on existing SSI's.<sup>75</sup>

Wet scrubber controls on SSI's range from low pressure drop spray towers and wet cyclones to higher pressure drop venturi scrubbers and venturi/impingement tray scrubber combinations. The most widely used control device applied to a multiple hearth incinerator is the impingement tray scrubber. Older units use the tray scrubber alone, while combination venturi/impingement tray scrubbers are widely applied to newer multiple hearth incinerators and to fluidized-bed incinerators. Most electric incinerators and some fluidized-bed incinerators use venturi scrubbers only.

In a typical combination venturi/impingement tray scrubber, hot gas exits the incinerator and enters the precooling or quench section of the scrubber. Spray nozzles in the quench section cool the incoming gas, and the quenched gas then enters the venturi section of the control device. Venturi water is usually pumped into an inlet weir above the quencher. The venturi water enters the scrubber above the throat and floods the throat completely. Most venturi sections come equipped with variable throats to allow the pressure drop to be increased, thereby increasing PM efficiency. At the base of the flooded elbow, the gas stream passes through a connecting duct to the base of the impingement tray tower. Gas velocity is further reduced upon entry to the tower as the gas stream passes upward through the perforated impingement trays. Water usually enters the trays from inlet ports on opposite sides and flows across the tray. As gas passes through each perforation in the tray, it creates a jet that bubbles up the water and further entrains solid particles. At the top of the tower is a mist eliminator to reduce the carryover of water droplets in the stack effluent gas.

### 6.5.3 Emissions

The primary source of mercury emissions from sewage sludge incineration is the combustion gas exhaust stack. However, small quantities of mercury also may be emitted with the fugitive PM emissions generated from bottom and fly ash handling operations.

As a part of the recent update of AP-42, data have been developed on mercury emissions from SSI's. These data are summarized in Table 6-19.

TABLE 6-19. SUMMARY OF MERCURY EMISSION FACTORS  
FOR SEWAGE SLUDGE INCINERATORS

Incinerator type <sup>a</sup>	Control status <sup>b</sup>	Mercury emission factors	
		g/Mg dry sludge	10 <sup>-3</sup> lb/ton dry sludge
MH	CY	2.3	4.6
	CY/VS	1.6	3.2
	IS	0.97	1.9
	VS/IS	0.005	0.01
FB	VS/IS	0.03	0.06

Source: Reference 75.

<sup>a</sup>MH = multiple hearth; FB = fluidized bed.

<sup>b</sup>CY = cyclone; VS = venturi scrubbers; IS = impingement scrubber.

The emission factors in Table 6-19 should be used cautiously in that available data suggest that both mercury concentrations in sludge and control efficiencies vary widely. Mercury emissions from SSI's are limited by a NESHAP to 3,200 grams per 24 hours for an entire facility. All SSI's are required to conduct more frequent monitoring/testing if the facility emits 1,600 or more grams per 24 hours.

Total 1994 mercury emissions from sewage sludge incineration are estimated to be 0.86 Mg (0.94 tons); see Appendix A for details.

## 6.6 HAZARDOUS WASTE COMBUSTION

Based on a 1994 listing of hazardous waste incinerators, the EPA Office of Solid Waste estimates that there are 190 permitted or interim status incinerators, 41 cement kilns, and 11 light-weight aggregate kilns that burn hazardous waste in the United States. Of these facilities, the commercial operations burn about 635,200 Mg (700,000 tons) of hazardous waste per year. The remaining facilities are onsite or captive units and burn about 726,000 Mg (800,000 tons) per year.<sup>81,82</sup> The incinerators generally utilize one of five basic technologies depending upon the types of waste to be treated: liquid injection, gas or fume, fixed or multiple hearth, rotary kiln, and fluidized bed. Of these, the liquid injection and rotary kiln are probably the two most prevalent types of incinerators currently in use.<sup>81</sup>

Lightweight aggregate kilns process a wide variety of raw materials (such as clay, shale, or slate) which, after thermal processing, can be combined with cement to form concrete products. Lightweight aggregate concrete is produced either for structural purposes or for thermal insulation purposes. A lightweight aggregate plant is typically composed of a quarry, a raw material preparation area, a kiln, a cooler, and a product storage area. The material is taken from the quarry to the raw material preparation area and from there is fed into the rotary kiln.

The sections below provide a description of the hazardous waste combustion process and types of incinerators and light-weight aggregate kilns, a discussion of control measures, and a summary of mercury emissions and factors. A discussion of the production of Portland cement, cement kiln control measures, and mercury emission sources is presented in Section 7.1. The mercury emission estimates discussed in Section 7.1 are for the use of nonhazardous waste fuel.

### 6.6.1 Process Description

**6.6.1.1 Incinerators.** In most processes, the waste to be treated is transported from a storage area to the incinerator where thermal oxidation occurs. Solid wastes are typically transported in drums or similar containers, and liquids or gases are piped from the storage area. Depending upon the type of incinerator and the wastes to be treated, either solid or liquid wastes or a combination may be fed into the incinerator along with an auxiliary (supplemental) fuel and combustion air. Unburned residual ash is removed from the incinerator, usually on a continuous basis, and is disposed. A portion of the noncombustible waste, as well as small amounts of unburned volatile organic material, are carried out of the primary incinerator chamber through entrainment in the exhaust gas stream. For some units (e.g., rotary kilns), the exhaust gas passes through a secondary combustion chamber (afterburner) before going to the air pollution control devices. Air pollution control devices, typically wet scrubbers, fabric filters, or electrostatic precipitators, are used to remove the entrained pollutants from the exhaust gas stream. The gas stream exits to the atmosphere through a stack, and the pollutants collected by the control devices are disposed. Scrubber effluents from the control devices are sent to wastewater treatment and solids from fabric filters typically are landfilled. Because of the high temperature in the combustion chambers, the primary source of mercury emissions from hazardous waste incineration is the stack; concentrations in the ash residue are expected to be very small. Some fugitive emissions may be generated during ash handling but the quantities also are expected to be very small.

The five basic incinerator types used in the United States are discussed in the following paragraphs. Two of the types, fixed (or multiple hearth) and fluidized bed, were described in the previous section on sewage sludge incinerators (Section 6.5.1) and will not be repeated here. The only major difference between their use for dewatered sewage sludge and hazardous waste may be differences in combustion temperatures; otherwise the units are essentially the same. The three designs discussed below are liquid injection, gas or fume, and rotary kilns.<sup>83</sup>

The liquid injection is one of the most common designs. In this design, a pumpable and atomizable waste is delivered to the incinerator and passes through burners into the combustion chamber. Burners consist of an atomizing nozzle and a turbulent mixing section where the waste is mixed with primary air. The incineration chamber is rectangular or cylindrical in shape, lined with refractory, and oriented vertically or horizontally. Vertically aligned chambers may be fired from either the top or bottom. Atomized waste is combusted at temperatures ranging from 870° to 1200°C (1300° to 3000°F) and residence times from 0.5 to 3 seconds. If the heat content of the liquid waste is insufficient to maintain the required combustion temperature, an auxiliary (supplemental) fuel is used. Following combustion, the exhaust gases pass through air pollution control devices and exit a stack.<sup>83</sup>

Gas or fume incinerators are very similar to liquid injection types except the treated waste is a gas or volatilized material (fume) instead of an atomized liquid. These incinerators are the simplest type to design and operate. Waste storage and pumping systems are designed for particular gas temperature/pressure considerations. The incinerator combustion chamber, combustion temperatures, and exhaust gas control devices are comparable to liquid injection systems.<sup>83</sup>

Rotary kiln incinerators generally are considered to be the most versatile and durable of the common types of incinerators. Using a mix to maintain necessary heat content, rotary kilns can simultaneously treat solid wastes, liquid organic wastes, and aqueous wastes. A rotary kiln is a refractory lined cylindrical steel shell tilted on the horizontal axis. The shell is usually supported on two or more steel tracks (trundles), which band the shell, and ride on rollers to allow the kiln to rotate around its horizontal axis. Waste material is tumbled through the kiln by gravity as the kiln rotates at a rate of 1 to 2 revolutions per minute. The rate of rotation and angle of tilt determine the solids residence time in the kiln. Rotary kiln diameters range from 1.2 to 4.9 meters (4 to 16 feet), and length-to-diameter ratios are typically 5:1. The kilns typically operate at temperatures of 870° to 980°C (1600° to 1800°F).<sup>83</sup>

In rotary kilns, solid waste is fed through the nonrotating upper end of the kiln using an auger screw or ram feeder. Pumpable wastes (e.g., sludges) can be fed through a water-cooled tube (wand) and liquid organic wastes, aqueous wastes, and/or auxiliary fuel are injected through burner nozzles. Waste continues to heat and burn as it travels down the inclined kilns. Combustion air is provided through ports on the face of the kiln; the kiln usually operates at 50 to 200 percent excess air. At the end of the kiln, the residual ash drops into an ash pit, is cooled, and removed for disposal. The exhaust gases, containing unburned components, are routed to an afterburner (secondary combustion chamber) operating at about 1100° to 1400°C (2000° to 2500°F) and 100 to 200 percent excess air. Auxiliary fuel and/or pumpable liquid wastes usually are used to maintain the afterburner temperature. The flue gases leave the afterburner, pass through air pollution control devices, and exit to the atmosphere through a stack.<sup>83</sup>

**6.6.1.2 Lightweight Aggregate Kilns.** A rotary kiln consists of a long steel cylinder, lined internally with refractory bricks, which is capable of rotating about its axis and is inclined at an angle of about 5 degrees to the horizontal. The length of the kiln depends in part upon the composition of the raw material to be processed but is usually 30 to 60 meters (98 to 197 feet). The prepared raw material is fed into the kiln at the higher end, while firing takes place at the lower end. The dry raw material fed into the kiln is initially preheated by hot combustion gases. Once the material is preheated, it passes into a second furnace zone where it melts to a semiplastic state and begins to generate gases which serve as the bloating or expanding agent. In this zone, specific compounds begin to decompose and form gases such as SO<sub>2</sub>, CO<sub>2</sub>, SO<sub>3</sub>, and O<sub>2</sub> that eventually trigger the desired bloating action within the material. As temperatures reach their maximum (approximately 1150°C [2100°F]), the semiplastic raw material becomes viscous and entraps the expanding gases. This bloating action produces small, unconnected gas cells, which remain in the material after it cools and solidifies. The product exits the kiln and enters a section of the process where it is cooled with cold air and then conveyed to the discharge.

Kiln operating parameters such as flame temperature, excess air, feed size, material flow, and speed of rotation vary from plant to plant and are determined by the characteristics of the raw material. Maximum temperature in the rotary kiln varies from about 1120°C to 1260°C (2050°F to 2300°F), depending on the type of raw material being processed and its moisture content. Typical exit temperatures may range from about 427° to 650°C (800° to 1200°F), again depending on the raw material and on the kiln's internal design. Approximately 50 to 200 percent excess air is forced into the kiln to aid in expanding the raw material.

## 6.6.2 Emission Control Measures

Incinerators are equipped with a wide variety of air pollution control devices (APCDs) that range in complexity from no control to complex, state-of-the-art systems that provide control for several pollutants. Units with no controls are limited to devices burning low ash and low chlorine content wastes. The hot flue gases from the incinerators are cooled and purged of air pollutants before exiting through the stack to the atmosphere. Cooling is done primarily by water quenching; water is atomized and sprayed directly into the hot flue gases. The cooled gases then pass through various APCDs to control particular matter (PM), acid gases, metals (including mercury), and organic components. Common APCDs for gaseous pollutant control include packed towers, spray dryers, and dry scrubbers; of these, packed towers are the most common. For PM control, venturi scrubbers, wet or dry electrostatic precipitators (ESPs), or fabric filters are common controls. Activated carbon injection is being used at one facility for control of dioxins and mercury.<sup>83</sup>

Lightweight aggregate kilns may use one or a combination of air pollution control devices, including fabric filters, venturi scrubbers, cyclones and dry scrubbers. All of the facilities utilize fabric filters as the main type of emissions control, although a spray dryer, venturi scrubber and dry scrubber may be used in addition to a fabric filter.

One of the major factors in control of mercury emissions is reduction of the flue gas temperature. Because wet scrubbing systems provide gas cooling as well as PM control, they can potentially provide some degree of mercury removal. Wet APCD devices, such as packed towers, wet ESPs, and high pressure drop venturi scrubbers, would be expected to show some degree of mercury control. Fabric filters would not be expected to show significant mercury reduction because of the high flue gas temperature.

### 6.6.3 Emissions

The principal source of mercury emissions from hazardous waste incinerators and lightweight aggregate kilns is the flue gas (combustion gas) exhaust stack. Small quantities of mercury compounds also may be emitted with fugitive PM emissions generated from incinerator ash handling operations.

As a part of the EPA proposed revised standards for hazardous waste combustors, baseline national emissions estimates were made for hazardous air pollutant (HAP) emissions, including mercury, from hazardous waste incinerators.<sup>81</sup> The baseline estimate entailed estimation of mercury emissions from the 78 hazardous waste incinerators in the EPA Office of Solid Waste (OSW) data base and then determination of the number of facilities not represented by the OSW data base. For facilities contained in the OSW data base, mercury average hourly emissions and stack gas flow rates (lb/hr) were calculated for each incinerator with emission measurements. Similar but untested units were assumed to have the same emission rate as tested units. The total number of units not represented in the OSW data base was determined and multiplied by the average mercury emission rate to obtain a total hourly mercury emission rate. Based on these data, an average mercury baseline emission rate was calculated for incinerators. Using similar calculations, an average mercury baseline emission rate for cement kilns and light-weight aggregate kilns was also calculated. Details on the methodologies used to estimate the mercury emissions from hazardous waste incinerators, cement kilns, and lightweight aggregate kilns may be obtained from docket materials prepared by the EPA Office of Solid Waste for the proposed hazardous waste combustion MACT standards.

Total 1996 mercury emissions from hazardous waste combustion are estimated to be 6.3 Mg (6.9 tons); see Appendix A for details.

## 6.7 MEDICAL WASTE INCINERATION

Medical waste includes infectious and noninfectious wastes generated by a variety of facilities engaged in medical care, veterinary care, or research activities such as hospitals, clinics, doctors' and dentists' offices, nursing homes, veterinary clinics and hospitals, medical laboratories, and medical and veterinary schools and research units. Medical waste is defined by the EPA as "any solid waste which is generated in the diagnosis, treatment, or immunization of human beings or animals, in research pertaining thereto, or in the production or testing of biologicals." A medical waste incinerator (MWI) is any device that burns such medical waste.<sup>84</sup> Based on comments received following proposal of the new source performance standards (NSPS) and emission guidelines (EG) for MWI's, EPA may elect to modify this definition by making it more specific.<sup>85</sup>

In the 1993 mercury document, estimates developed by EPA suggested that about 3.06 million Mg (3.36 million tons) of medical waste were produced annually in the United States.<sup>32</sup> The EPA estimated that approximately 5,000 MWI's located at hospitals, veterinary facilities, nursing homes, laboratories, and other miscellaneous facilities across the U.S. were used to treat this waste.<sup>86</sup> Following proposal of the NSPS and EG for new and existing MWI's, the EPA received new information regarding the number of MWI's operating throughout the United States. More recent estimates developed for the MWI EG indicate that there are approximately 2,400 MWI's operating in the United States. These 2,400 MWI's are used to treat approximately 767 thousand Mg (846 thousand tons) of medical waste per year. The lower estimate of the number of existing MWI's operating in the U.S. has led to a lower estimate of the mercury emissions produced by MWI's. The EPA currently estimates that MWI's emit approximately 14.5 Mg (16.0 tons) of mercury per year. However, the upcoming EG are expected to reduce mercury emissions by more than 90 percent.<sup>85</sup>

Available information indicates that MWI systems can be significant sources of mercury emissions. Mercury emissions result from mercury-bearing materials contained in the waste. Although concentrations of specific metals in the waste have not been fully characterized, known mercury sources include batteries; fluorescent lamps; high-intensity discharge lamps (mercury vapor, metal halide, and high-pressure sodium); thermometers; special paper and film coatings; and pigments. Prior to 1991, batteries, primarily alkaline and mercury-zinc batteries, were a major mercury source. Prior to 1991, the concentration of mercury in alkaline batteries was about 1 percent and that of mercury-zinc batteries ranged from 35 to 50 percent mercury. In 1991, several battery manufacturers reduced the mercury content in alkaline batteries to less than 0.025 percent. Additionally, the use of zinc-air batteries as a replacement for the mercury-zinc batteries became more prevalent. Alkaline batteries are general purpose batteries that are used in a variety of equipment. Mercury-zinc batteries previously were used in transistorized equipment, hearing aids, watches, calculators, computers, smoke detectors, tape recorders, regulated power supplies, radiation detection meters, scientific equipment, pagers, oxygen and metal monitors, and portable electrocardiogram monitors. Cadmium-mercury pigments are primarily used in plastics but also are used in paints, enamels, printing inks, rubber, paper, and painted textiles.<sup>69,87</sup> Hospital laboratory facilities use polyvinyl alcohol (PVA) fixatives to preserve and examine stool specimens for internal parasites; these diagnostic tools contain mercuric chloride and may be disposed in the MWI waste stream. All of these materials can be routed to an MWI, thereby contributing to mercury emissions from this source category.

#### 6.7.1 Process Description

Although the ultimate destination of almost all medical waste produced in the United States is a solid waste landfill, the waste generally must be treated before it can be landfilled. The primary functions of MWI facilities are to render the waste biologically innocuous and to reduce the volume and mass of solids that must be landfilled by combusting the organic material contained in the waste. Over the years, a wide variety of MWI system designs and operating practices have been used to accomplish these functions. To account for these system differences, a number of MWI classification schemes have been used in past studies, including classification by waste type (pathological, mixed medical waste, red bag waste, etc.), by operating mode (continuous, intermittent, batch), and by combustor design (retort, fixed-hearth, pulsed-hearth, rotary kiln, etc.). Some insight into MWI processes, emissions, and emissions control is provided by each of these schemes. However, because the available evidence suggests that mercury emissions are affected primarily by waste characteristics, the characterization and control of mercury emissions from MWI's can be discussed without considering other MWI design and operating practices in detail. The paragraphs below provide a generic MWI process description and identify potential sources of mercury emissions.

A schematic of a generic MWI system that identifies the major components of the system is shown in Figure 6-2. As indicated in the schematic, most MWI's are multiple-chamber combustion systems that comprise primary, secondary, and possibly tertiary chambers. The primary components of the MWI process are the waste-charging system, the primary chamber, the ash handling system, the secondary chamber, and the air pollution control system, which are discussed briefly below.

Medical waste is introduced to the primary chamber via the waste-charging system. The waste can be charged either manually or mechanically. With manual charging, which is used only on batch and smaller (generally older) intermittent units, the operator opens a charge door on the side of the primary chamber and tosses bags or boxes of waste into the unit. When mechanical feed systems are employed, some type of mechanical device is used to charge the waste to the incinerator. The most common mechanical feed system is the hopper/ram assembly. In a mechanical hopper/ram feed system, the following steps occur: (1) waste is placed into a charging hopper manually, and the hopper cover is closed; (2) a fire door isolating the hopper from the incinerator opens; (3) the ram moves forward to push the waste into the incinerator; (4) the ram reverses to a location behind the fire door; and (5) after the fire door closes, a water spray cools the ram, and the ram retracts to the starting position. The system now is ready to accept another charge. The entire hopper/ram charging sequence normally functions as a controlled, automatically-timed sequence to eliminate overcharging. The sequence can be activated by the

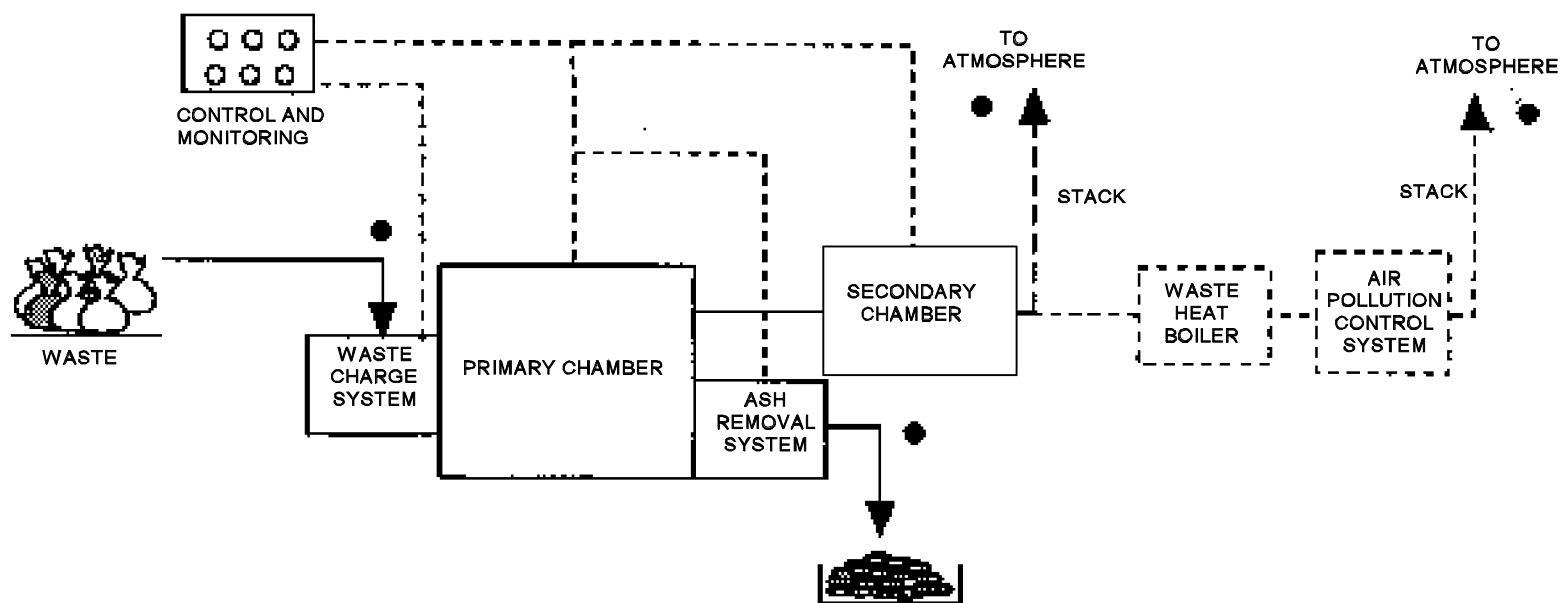


Figure 6-2. Major components of an incineration system.

operator or for larger, fully automated incinerators, it may be activated at preset intervals by an automatic timer.<sup>88,89</sup>

The potential for mercury emissions from the waste-charging systems is low. Mechanical systems are generally operated with a double-door system to minimize fugitive emissions. Small quantities of fugitive emissions may be generated while the chamber door is open during manual charging, but no data are available on the magnitude of these emissions.

The primary chamber (sometimes called the "ignition" chamber) accepts the waste and begins the combustion process. Most modern MWI's operate this chamber in a "controlled-air" mode to maintain combustion air levels at or below stoichiometric requirements. The objectives of this controlled-air operation are to provide a more uniform release of volatile organic materials to the secondary chamber and to minimize entrainment of solids in these off-gases. Three processes occur in the primary chamber. First, the moisture in the waste is volatilized. Second, the volatile fraction of the waste is vaporized, and the volatile gases are directed to the secondary chamber. Third, the fixed carbon remaining in the waste is combusted.

The primary chamber generates two exhaust streams--the combustion gases that pass to the secondary chamber and the solid ash stream that is discharged. Any metal compounds in the waste, including mercury, are partitioned to these two streams in one of three ways. The metals may be retained in the primary chamber bottom ash and discharged as solid waste; they may be entrained as PM in the combustion gases; or they may be volatilized and discharged as a vapor with the combustion gases. Because mercury and mercury compounds are generally quite volatile and because the primary chamber typically operates in the range of 650° to 820°C (1200° to 1500°F), most of the mercury in the waste stream will be exhausted as a vapor to the secondary chamber.

The primary chamber bottom ash, which may contain small amounts of mercury or mercury compounds, is discharged via an ash removal system and transported to a landfill for disposal. The ash removal system may be either manual or mechanical. Typically, batch units and smaller intermittent units employ manual ash removal. After the system has shut down and the ash has cooled, the operator uses a rake or shovel to remove the ash and place it in a drum or dumpster. Some intermittent-duty MWI's and all continuously operated MWI's use a mechanical ash removal system. The mechanical system includes three major components: (1) a means of moving the ash to the end of the incinerator hearth--usually an ash transfer ram or series of transfer rams, (2) a collection device or container for the ash as it is discharged from the hearth, and (3) a transfer system to move the ash from the collection point. Generally, these automatic systems are designed to minimize fugitive emissions. For example, one type of collection system uses an ash bin sealed directly to the discharge chute or positioned within an air-sealed chamber below the hearth. A door or gate that seals the chute is opened at regular intervals to allow the ash to drop into the collection bin. When the bin is filled, the seal-gate is closed, and the bin is removed and replaced with an empty bin. In another system, the ash is discharged into a water pit. The ash discharge chute is extended into the water pit so that an air seal is maintained. The water bath quenches the ash as the ash is collected. A mechanical device, either a rake or drag conveyor system, is used to intermittently or continuously remove the ash from the quench pit. The excess water is allowed to drain from the ash as it is removed from the pit, and the wetted ash is discharged into a collection container.

The potential for mercury emissions from both mechanical and manual ash discharge systems is minimal. As described above, most mechanical systems have seals and provide ash wetting as described above to minimize fugitive PM emissions. While manual systems can generate substantial fugitive PM, the concentrations of mercury have generally been shown to be quite low.<sup>90</sup> Consequently, fugitive mercury emissions are negligible.

The primary function of the secondary chamber is to complete the combustion of the volatile organic compounds that was initiated in the primary chamber. Because the temperatures in the secondary chamber are typically 980°C (1800°F) or greater, essentially all of the mercury that enters the secondary chamber will be exhausted as a vapor. The hot exhaust gases from the secondary chamber may pass through an energy recovery device (waste heat boiler or air-to-air heat exchanger) and an air pollution control system before they are discharged to the atmosphere through the combustion stack. This combustion stack is the major route of mercury emissions from MWI's.



### 6.7.2 Emission Control Measures

A number of air pollution control system configurations have been used to control PM and gaseous emissions from the MWI combustion stacks. Most of these configurations fall within the general classes of wet systems and dry systems. Wet systems typically comprise a wet scrubber designed for PM control (venturi scrubber or rotary atomizing scrubber) in series with a packed-bed scrubber for acid gas removal and a high-efficiency mist elimination system. Most dry systems use a fabric filter for PM removal, but ESP's have been installed on some larger MWI's. These dry systems may use sorbent injection via either dry injection or spray dryers upstream from the PM device to enhance acid gas control. Additionally, some systems incorporate a combination dry/wet system that comprises a dry sorbent injection/fabric filter system followed by a venturi scrubber. Because the systems described above are designed primarily for PM and acid gas control, they have limitations relative to mercury control. However, recent EPA studies indicate that sorbent injection/fabric filtration systems can achieve improved mercury control by adding activated carbon to the sorbent material. The emission data presented in the section below provide information on the performance of some of the more common systems.

### 6.7.3 Emissions

The primary source of emissions from medical waste incineration is the combustion gas exhaust stack. However, small quantities of mercury may be contained in the fugitive PM emissions from ash handling operations, particularly if the fly ash is collected in a dry air pollution control system with high mercury removal efficiencies.

Over the past 8 years, mercury emissions have been measured at several MWI's through the EPA's regulatory development program, MWI emission characterization studies conducted by the State of California, and compliance tests conducted in response to State air toxic requirements. In the 1993 mercury L&E document, mercury emission data were available from 20 MWI's. Of these, data from 14 of the facilities were considered to be adequate for emission factor development.<sup>32</sup> Since publication of the previous document, an additional 27 emission test reports were obtained by EPA to be used in the reassessment of the performance of add-on air pollution control devices (APCD's). These test reports were reviewed by EPA's Emission Measurements Center (EMC) for completeness to determine if the test data was suitable for use in the development of the maximum achievable control technology (MACT) standards and guidelines for MWI's. The results of the EMC review are documented in a memorandum describing the general selection rules for MWI and APCD emission test data.<sup>91</sup>

Emission factors for MWI's with combustion controls, wet scrubbers, fabric filter/packed bed systems, and dry scrubbers (with and without activated carbon injection) were developed for the MWI standards and guidelines. The MWI emission factors were developed by (1) developing exhaust gas flow rate-to-waste burned factors (dscf/lb factors), (2) developing pollutant concentrations for each control technology, and (3) calculating emission factors by multiplying together the results of the first two steps. Approximately 26 emissions test reports, including those from EPA's emissions test program and test reports reviewed by EMC with sufficient process data, were used to develop the dscf/lb factors. The average dscf/lb factor for intermittent and continuous MWI's was determined to be 2.67 dscf/lb (at 7 percent O<sub>2</sub>).<sup>92</sup> The mercury emissions data from 19 emissions test reports (8 from EPA's emissions test program and 11 additional reports qualified by EMC) was used to determine the achievable emissions concentrations for MWI's with combustion controls, wet scrubbers, and dry scrubbers.<sup>93,94,95</sup> The emission factors for each control technology were calculated by multiplying the average dscf/lb factor by the achievable mercury concentration for each control technology.

Table 6-20 presents the MWI emission factors for each control technology developed by EPA for the MWI NSPS and EG. The emission factors presented in Table 6-20 are average emission factors that represent emissions from continuous and intermittent MWI's that burn a mixture of noninfectious waste and infectious (red bag) waste. While the procedure used to calculate the MWI emission factors provides average emission factors that represent the industry cross section, it should not be used to determine emission factors for individual facilities. The dscf/lb factor presented above may not be appropriate for specific facilities due to variations in auxiliary fuel usage and excess air ratios.

Total 1996 mercury emissions from medical waste incineration are estimated to be 14.5 Mg (16 tons); see Appendix A for details.

TABLE 6-20. MERCURY EMISSION FACTORS FOR MWI'S

Air pollution control	Mercury emission factor	
	g/Mg waste	10 <sup>-3</sup> lb/ton waste
Combustion control	37	74
Wet scrubber	1.3	2.6
Dry scrubber w/o carbon	37	74
Dry scrubber w/ carbon	1.7	3.3
Fabric filter/packed bed	1.3	2.6

## 7.0 EMISSIONS FROM MISCELLANEOUS SOURCES

Mercury has been found to be emitted from various miscellaneous sources including the following:

1. Portland cement manufacturing,
2. Lime manufacturing,
3. Carbon black production,
4. Byproduct coke production,
5. Primary lead smelting,
6. Primary copper smelting,
7. Petroleum refining,
8. Municipal solid waste landfills,
9. Geothermal power plants, and
10. Pulp and paper production.

Raw materials processed at the facilities listed above include minerals, ores, and crudes extracted from the earth. Many of these raw materials contain mercury. At various stages of processing, the raw materials are heated. Therefore, each of the manufacturing processes listed above may emit mercury during various steps of raw materials processing. A summary of the estimated mercury emissions from each of the above industries is as follows:

Industry	Emissions, Mg (tons)
Portland cement manufacture	4.0 (4.4)
Lime manufacture	0.1 (0.1)
Carbon black production	0.3 (0.3)
Byproduct coke production	0.6 (0.7)
Primary lead smelting	0.1 (0.1)
Primary copper smelting	0.06 (0.07)
Municipal solid waste landfills	0.07 (0.08)
Geothermal power plants	1.3 (1.4)
Pulp and paper production	1.6 (1.8)

No emission estimate was developed for petroleum refining because the only emission factors were for auxiliary processes not specifically associated with petroleum refining.

This section presents process information, air pollution control measures, and estimates of mercury emissions for these sources.

### 7.1 PORTLAND CEMENT MANUFACTURING

More than 30 raw materials are used to manufacture portland cement. These materials can be classified into four basic classes of raw materials: calcareous, siliceous, argillaceous, and ferriferous. Two processes, the wet and dry processes, can be used to manufacture portland cement. In 1995, there was a total of 208 U.S. cement kilns with a combined total clinker capacity of  $76.3 \times 10^6$  Mg ( $83.9 \times 10^6$  tons). Of this total, six kilns with a combined capacity of  $1.7 \times 10^6$  Mg ( $1.9 \times 10^6$  tons) were inactive. The total number of active kilns was 202 with a clinker capacity of  $74.7 \times 10^6$  Mg ( $82.2 \times 10^6$  tons).<sup>96</sup> The name, location, and clinker capacity (in metric tons) of each kiln is presented in Appendix C. Based on 1995 U.S. cement kiln capacity data, an estimated 72 percent of the portland cement is manufactured using the dry process, and the remaining 28 percent based on the wet process. A description of the processes used to manufacture portland cement and the emissions resulting from the various operations is presented below.<sup>97</sup>

### 7.1.1 Process Description

Figure 7-1 presents a basic flow diagram of the portland cement manufacturing process. The process can be divided into four major steps: raw material acquisition and handling, kiln feed preparation, pyroprocessing, and finished cement grinding.<sup>97</sup>

The initial step in the production of portland cement manufacturing is raw materials acquisition. Calcium, which is the element of highest concentration in portland cement, is obtained from a variety of calcareous raw materials, including limestone, chalk, marl, sea shells, aragonite, and an impure limestone known as "natural cement rock." The other raw materials--silicon, aluminum, and iron--are obtained from ores and minerals, such as sand, shale, clay, and iron ore. Mercury is expected to be present in the ores and minerals extracted from the earth. The only potential source of mercury emissions from raw material acquisition would be due to wind blown mercury-containing particulate from the quarry operations. Mercury emissions are expected to be negligible from these initial steps in portland cement production.

The second step involves preparation of the raw materials for pyroprocessing. Raw material preparation includes a variety of blending and sizing operations designed to provide a feed with appropriate chemical and physical properties. The raw material processing differs somewhat for wet- and dry-processes. At facilities where the dry process is used, the moisture content in the raw material, which can range from less than 1 percent to greater than 50 percent, is reduced to less than 1 percent. Mercury emissions can occur during this drying process but are anticipated to be very low because the drying temperature is generally well below the boiling point of mercury. However, some dryers do attain a temperature above the boiling point of mercury, which would react in emissions. At some facilities, heat for drying is provided by the exhaust gases from the pyroprocessor. At facilities where the wet process is used, water is added to the raw material during the grinding step, thereby producing a pumpable slurry containing approximately 65 percent solids.

Pyroprocessing (thermal treatment) of the raw material is carried out in the kiln, which is the heart of the portland cement manufacturing process. During pyroprocessing, the raw material is transformed into clinkers, which are gray, glass-hard, spherically-shaped nodules that range from 0.32 to 5.1 cm (0.125 to 2.0 in.) in diameter. The chemical reactions and physical processes that take place during pyroprocessing are quite complex. The sequence of events can be divided into four stages:

1. Evaporation of uncombined water from raw materials as material temperature increases to 100°C (212°F),
2. Dehydration as the material temperature increases from 100°C to approximately 430°C (800°F) to form the oxides of silicon, aluminum, and iron,
3. Calcination, during which carbon dioxide (CO<sub>2</sub>) is evolved, between 900°C (1650°F) and 982°C (1800°F) to form calcium oxide,
4. Reaction of the oxides in the burning zone of the rotary kiln to form cement clinker at temperatures about 1510°C (2750°F).

The rotary kiln is a long, cylindrical, slightly inclined, refractory-lined furnace. The raw material mix is introduced into the kiln at the elevated end, and the combustion fuels are usually introduced into the kiln at the lower end, in a countercurrent manner. The rotary motion of the kiln transports the raw material from the elevated end to the lower end. Fuel such as coal or natural gas, or occasionally oil, is used to provide energy for calcination. Mercury is present in coal and oil. Tables 6-4 and 6-11 presented data pertaining to mercury content in coal and oil, respectively. Use of other fuels, such as chipped rubber, petroleum coke, and waste solvents, is becoming increasingly popular. Combustion of fuel during the pyroprocessing step contributes to potential mercury emissions. Mercury may also be present in the waste-derived fuel mentioned above. Because mercury evaporates at approximately 350°C (660°F), most of the mercury present in the raw materials can be expected to be volatilized during the pyroprocessing step.

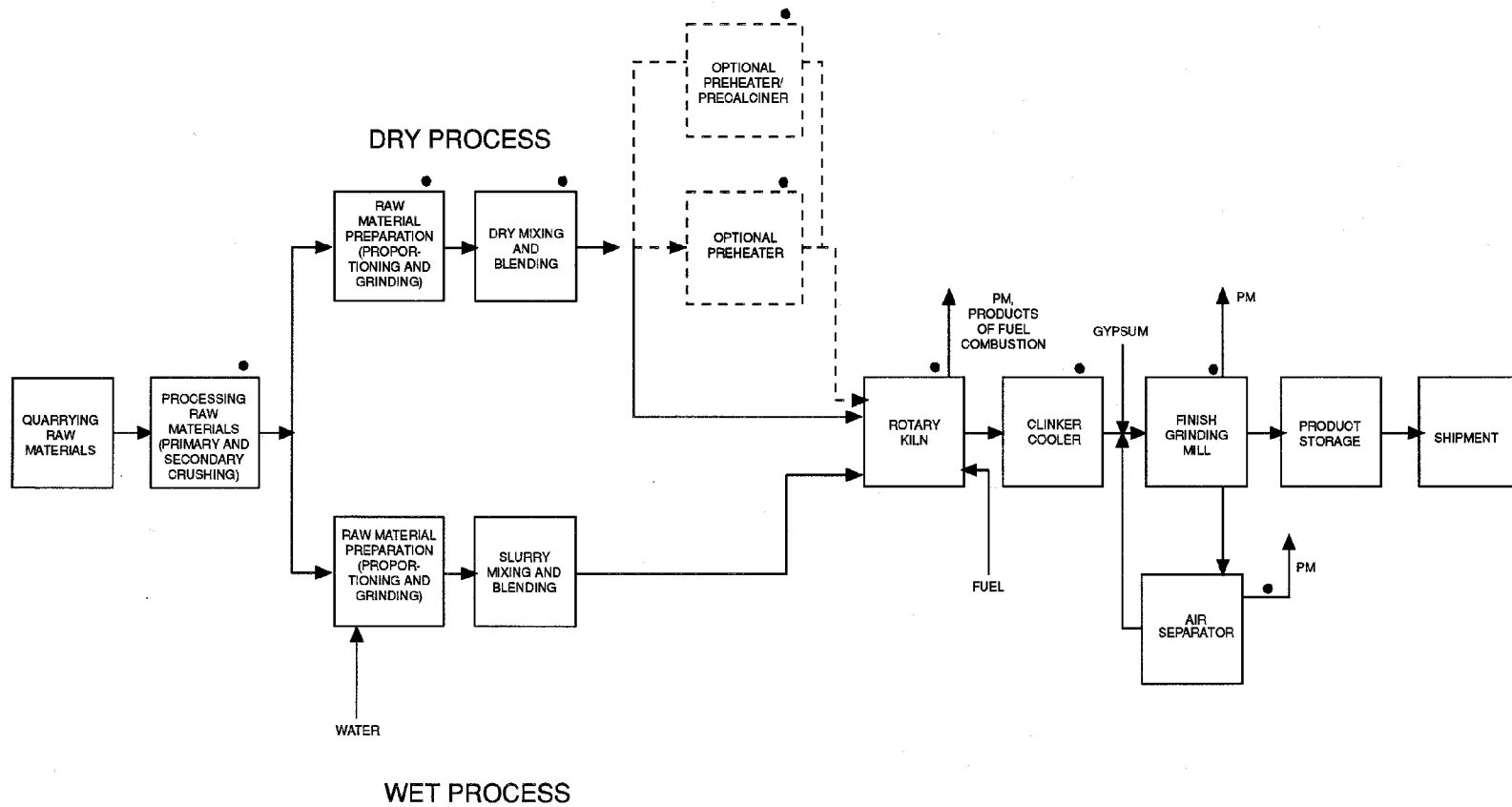


Figure 7-1. Process flow diagram of portland cement manufacturing process.<sup>97</sup>

Pyroprocessing can be carried out using one of five different processes: wet process, semi-dry, dry process, dry process with a preheater, and dry process with a preheater/precalciner. These processes essentially accomplish the same physical and chemical steps described above. The last step in the pyroprocessing is the cooling of the clinker. This process step recoups up to 30 percent of the heat input to the kiln system, locks in desirable product qualities by freezing mineralogy, and makes it possible to handle the cooled clinker with conventional conveying equipment. Finally, after the cement clinker is cooled, a sequence of blending and grinding operations is carried out to transform the clinker into finished portland cement.

#### 7.1.2 Emission Control Measures<sup>97</sup>

The primary pollutants resulting from the manufacture of portland cement are PM and PM-10, NO<sub>x</sub>, SO<sub>2</sub>, CO, and CO<sub>2</sub>. Emissions of metal compounds occur from the portland cement kilns and can be grouped into three general classes: volatile metals (including mercury), semivolatile metals, and refractory or nonvolatile metals. Although partitioning of the metals is affected by kiln operating conditions, the refractory metals tend to concentrate in the clinker, the semivolatile metals tend to be discharged through the bypass stack, and the volatile metals through the primary exhaust stack. The largest emission source of volatile metals within the cement plant is the pyroprocessing system that includes the kiln and clinker cooler exhaust stacks.

Process fugitive emission sources include materials handling and transfer, raw milling operations in dry process facilities, and finish milling operations. Potential mercury emission sources are indicated in Figure 7-1 by solid circles. Typically, particulate emissions from these processes are captured by a ventilation system with a fabric filter. Because the dust from these units is returned to the process, they are considered to be process units as well as air pollution control devices. The industry uses shaker, reverse air, and pulse jet filters, as well as some cartridge units, but most newer facilities use pulse jet filters. For process fugitive operations, the different systems are reported to achieve typical outlet PM loadings of 45 milligrams per cubic meter mg/m<sup>3</sup> (0.02 grains per actual cubic foot [gr/acf]). Because some fraction of the mercury is in particle form, the performance of these systems relative to particulate mercury control is expected to be equivalent to this overall particulate performance.

In the pyroprocessing units, PM emissions are controlled by fabric filters (reverse air, pulse jet, or pulse plenum) and ESP's. Clinker cooler systems are controlled most frequently with pulse jet or pulse plenum fabric filters. A few gravel bed (GB) filters have been used on clinker coolers.

The dust collected by the various fabric filters at the cement manufacturing facility is called cement kiln dust (CKD). This dust is typically recycled into the process as a feed ingredient and substantially passes through the cement kiln again, where a fraction of the residual mercury in the dust is volatilized. As dust is continually recycled, essentially all of the mercury input to the process will eventually leave the system as a vapor from the kiln stack. If the CKD is disposed, however, the particulate mercury remaining in the CKD also goes to disposal, and only the mercury volatilized during the single pass through the cement kiln escapes to the atmosphere as vapor from the kiln stack.

#### 7.1.3 Emissions

The mercury emissions discussed in this section for the manufacture of portland cement are only for the use of fossil fuels and nonhazardous waste auxiliary fuels. Mercury emissions from the use of hazardous waste fuels were discussed in Section 6.6, Hazardous Waste Combustion.

The principal sources of mercury emissions are expected to be from the kiln and preheating/precalcining steps. Negligible quantities of emissions would be expected in the raw material processing and mixing steps because the only source of mercury would be fugitive dust containing naturally occurring quantities of mercury compounds from the raw materials. Processing steps that occur after the calcining process in the kiln would be expected to be a much smaller source of emissions than the kiln. Potential mercury emission sources are denoted by solid circles in Figure 7-1. Emissions resulting from all processing steps include particulate matter. Additionally, emissions from the pyroprocessing step include other products of fuel combustion such as SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, and CO. Carbon dioxide from the calcination of limestone will also be present in the flue gas.

Cement kiln test reports have been reviewed by EPA (and its contractor) in its development of the portland cement industry NESHAP, and by a private company. Test reports for Certification of Compliance (COC) emissions tests (required of all kilns burning hazardous waste derived fuel) (WDF) and test reports for facilities not burning hazardous waste were reviewed.<sup>98,99</sup> The results from the Gossman study showed an average emission factor of  $0.65 \times 10^{-4}$  kg/Mg of clinker ( $1.3 \times 10^{-4}$  lb/ton of clinker) for nonhazardous waste fuels. The RTI study evaluated tests based on both nonhazardous waste fuel and hazardous waste fuel. For the hazardous waste tests, the mercury emissions data were corrected to reflect only the mercury emissions originating from the fossil fuel and raw material. The emissions data for nonhazardous waste and the corrected hazardous waste were combined and showed an average mercury emission factor of  $0.65 \times 10^{-4}$  kg/Mg of clinker ( $1.29 \times 10^{-4}$  lb/ton of clinker).

Total 1994 mercury emissions from this industry are estimated to be 4.0 Mg (4.4 tons); see Appendix A for details.

## 7.2 LIME MANUFACTURING

Lime is produced in various forms, with the bulk of production yielding either hydrated lime or quicklime. In 1994, producers sold or used  $17.4 \times 10^6$  Mg ( $19.2 \times 10^6$  tons) of lime produced at 109 plants in 33 States and Puerto Rico. The 1994 production represented a 3.6 percent increase over 1993 production. In 1990, there were 113 lime production operations in the U.S. with a annual production of  $15.8 \times 10^6$  Mg ( $17.4 \times 10^6$  tons). The leading domestic uses for lime include steelmaking, pulp and paper manufacturing, and treatment of water, sewage, and smokestack emissions.<sup>100</sup>

Appendix C provides a list of the active lime plants in the United States in 1991. The list includes company headquarters' locations, plant locations by State, and the type of lime produced at each plant. The geographical locations, by State, of the lime operations and quantities of lime produced are shown in Table 7-1.

### 7.2.1 Process Description

Lime is produced by calcining (removal of  $\text{CO}_2$ ) limestone at high temperature. Limestone is commonly found in most states but only a small portion can be used for lime production. To be classified as limestone, the rock must contain 50 percent or more calcium carbonate. If the rock contains 30 to 45 percent magnesium carbonate, it is called dolomite. The product of the calcining operation is quicklime; this material can be hydrated with water to produce hydrated lime or slaked lime ( $\text{Ca}(\text{OH})_2$ ). The product of calcining dolomite is dolomitic quicklime; it also can be hydrated. Figure 7-2 presents a flow diagram for the lime manufacturing process. Lime manufacturing is carried out in five major steps. These are:

1. Quarrying raw limestone,
2. Preparing the limestone for calcination,
3. Calcining the limestone,
4. Processing the lime by hydrating, and
5. Miscellaneous transfer, storage, and handling processes.

The manufacturing steps in lime production are very similar to that of the dry portland cement process, which was discussed in the previous section. The most important process step with respect to emissions of mercury and other air pollutants is the calcination. During calcination, kiln temperature may reach  $1820^\circ\text{C}$  ( $3300^\circ\text{F}$ ). Approximately 90 percent of the lime produced in the United States is manufactured by calcining limestone in a rotary kiln. Other types of lime kilns include the vertical or shaft kiln, rotary hearth, and fluidized bed kilns. Fuel, such as coal, oil, petroleum coke, or natural gas, may be used to provide energy for calcination. Petroleum coke is usually used in combination with coal; oil is rarely used as a fuel source. Approximately one-third of the U.S. lime kilns are fired with natural gas. Auxiliary fuels such as chipped rubber and waste solvents may potentially be used; at the present time, however, no lime kilns use these auxiliary fuels.<sup>101</sup>

Mercury is expected to be present in very small quantities in the limestone and in coal and oil used as fuel. Data pertaining to the mercury content in coal and oil are presented in Sections 6.1 and 6.2, respectively. As with the production of portland cement, any mercury present in the raw materials can be

TABLE 7-1. LIME PRODUCERS IN THE UNITED STATES IN 1994

State	No. of plants	Lime production x 10 <sup>3</sup> Mg (x10 <sup>3</sup> tons)					
		Hydrated <sup>a</sup>		Quicklime <sup>a</sup>		Total <sup>a</sup>	
Alabama	4	184	(203)	1,470	(1,620)	1,660	(1,829)
Arizona, Nevada, Utah	8	243	(268)	1,570	(1,730)	1,810	(1,995)
California	7	26	(29)	178	(196)	203	(224)
Colorado, Montana, Wyoming	10	--	(--)	335	(369)	335	(369)
Idaho, Oregon, Washington	8	25	(28)	597	(658)	622	(685)
Illinois, Indiana, Missouri	8	464	(511)	2,910	(3,207)	3,380	(3,725)
Iowa, Nebraska, South Dakota	5	W	(W)	W	(W)	(242)	(267) <sup>b</sup>
Kentucky, Tennessee, West Virginia	5	132	(145)	1,800	(1,984)	1,930	(2,127)
Michigan	9	26	(29)	611	(673)	637	(702)
North Dakota	3	--	(--)	108	(119)	108	(119)
Ohio	9	W	(W)	W	(W)	(1,850)	(2,039) <sup>c</sup>
Pennsylvania	8	263	(290)	1,330	(1,466)	1,590	(1,752)
Puerto Rico	1	23	(25)	<0.5	(<0.6)	23	(25)
Texas	6	471	(519)	740	(815)	1,210	(1,333)
Virginia	5	121	(133)	621	(684)	742	(818)
Wisconsin	4	124	(137)	383	(422)	507	(559)
Other <sup>d</sup>	9	213	(235)	2,430	(2,678)	2,640	(2,909)
Total	109	2,310	(2,546)	15,100	(16,640)	17,400	(19,175)

Source: Reference 100.

<sup>a</sup>Metric ton data rounded by the U.S.G.S. to three significant digits; may not add to totals shown.<sup>b</sup>Withheld to avoid disclosing company proprietary data; included in "Other" category.<sup>c</sup>Total included in total for "Other" category.<sup>d</sup>Includes Arkansas, Louisiana, Massachusetts, Minnesota, Oklahoma, and data indicated by "W".



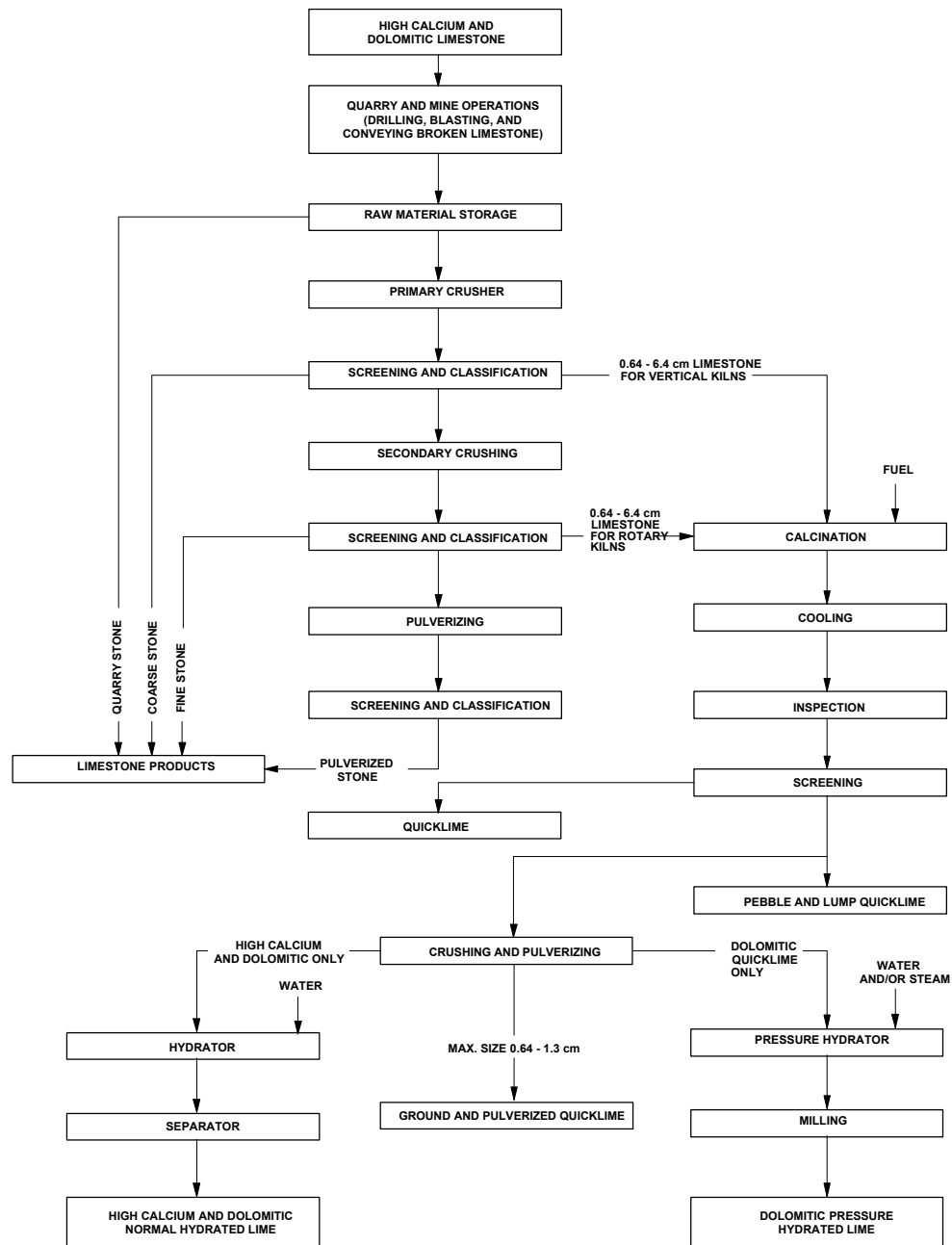


Figure 7-2. Process flow diagram for lime manufacturing process.<sup>101</sup>

expected to be emitted in the lime kiln. Combustion of fuel in the lime kiln is the major contributor to mercury emissions.

### 7.2.2 Emission Control Measures

With the exception of the lime kiln, the emission sources in the lime manufacturing industry can be classified as either process emissions or fugitive emissions. The primary pollutants resulting from these fugitive sources are PM. No specific control measures for the lime industry are reported in the literature for the fugitive sources. The reduction measures used for fugitive dust sources at portland cement manufacturing facilities may also be applicable at lime manufacturing industries.

Air pollution control devices for lime kilns are primarily used to recover product or control fugitive dust and PM emissions. Calcination kiln exhaust is typically routed to a cyclone for product recovery, and then routed through a fabric filter or ESP's to collect fine particulate emissions. Other emission controls found at lime kilns include wet scrubbers (typically venturi scrubbers). How well these various air pollution control devices perform, relative to vapor phase mercury emissions in lime production, is not well documented. The control efficiencies are expected to be similar to those observed in the production of portland cement because of the similarities in the process and control devices.

### 7.2.3 Emissions

Mercury emissions from fuel combustion will occur from the lime kiln (calcination) as shown in Figure 7-2. Mercury present in the limestone will also be emitted from the kiln. All other potential emission sources in the process are expected to be very minor contributors to overall mercury emissions. Emissions resulting from all five processing steps include particulate matter. Additionally, emissions from the lime kiln include other products of fuel combustion such as SO<sub>2</sub>, NO<sub>x</sub>, CO, and CO<sub>2</sub>.

Lime kiln test reports are available for two facilities in the United States and one in Canada. The source test reports for the U. S. facilities have been reviewed by EPA ( and its contractor) in its development of the lime manufacturing industry NESHAP.<sup>102</sup> The test report for the Canadian facility was provided by the National Lime Association and reviewed as a part of this document.<sup>103</sup> At the Canadian facility, two different kilns were tested; one was a coal/coke-fired rotary kiln and the other was a natural gas-fired vertical kiln. For the coal/coke-fired rotary kiln, the results from the tests showed an average mercury emission factor of  $9.0 \times 10^{-6}$  kg/Mg of lime produced ( $1.8 \times 10^{-5}$  lb/ton of lime produced); the emission factors ranged from  $0.8 \times 10^{-5}$  to  $1.0 \times 10^{-5}$  kg/Mg of lime produced ( $1.6 \times 10^{-5}$  to  $2.0 \times 10^{-5}$  lb/ton of lime produced) over the four test runs. For the natural gas-fired vertical kiln, the results showed an average mercury emission factor of  $1.5 \times 10^{-6}$  kg/Mg of lime produced ( $3.0 \times 10^{-6}$  lb/ton of lime produced); the emission factors ranged from  $1.45 \times 10^{-6}$  to  $1.6 \times 10^{-6}$  kg/Mg of lime produced ( $2.9 \times 10^{-6}$  to  $3.2 \times 10^{-6}$  lb/ton of lime produced) over the four test runs. Process data from the tests at the Canadian facility were used to calculate the quantity of limestone fed required to produce 0.91 Mg (1.0 ton) of lime. Based on process data for the rotary kiln, the average ratio of limestone feed to lime produced was 0.50 (i.e., 2 tons of limestone are required to produce 1 ton of lime). The average ratio for the vertical kiln was calculated to be 0.51.

The test results from the two U. S. facilities were evaluated for EPA by its contractor, TRI. Both of the facilities, APG Lime Company and Eastern Ridge Lime company, employed coal-fired rotary kilns. The results of the tests at APG showed an average mercury emission factor of  $1.9 \times 10^{-6}$  kg/Mg of limestone feed ( $3.8 \times 10^{-6}$  lb/ton of limestone feed). Based on the 2:1 limestone feed to lime produced ratio, this corresponds to an emission factor of  $3.8 \times 10^{-6}$  kg/Mg of lime produced ( $7.6 \times 10^{-6}$  lb/ton of lime produced). At Eastern Ridge, the results showed an average mercury emission factor of  $4.7 \times 10^{-6}$  kg/Mg of limestone feed ( $9.4 \times 10^{-6}$  lb/ton of limestone feed). Using the 2:1 conversion ratio, this corresponds to a mercury emission factor of  $9.4 \times 10^{-6}$  kg/Mg of lime produced ( $1.9 \times 10^{-5}$  lb/ton of lime produced). The average mercury emission factors for the coal-fired rotary kilns from the one Canadian facility and the two U. S. facilities were combined and showed an overall average mercury emission factor of  $7.4 \times 10^{-6}$  kg/Mg of lime produced ( $1.5 \times 10^{-5}$  lb/ton of lime produced).

The total 1994 mercury emissions from this industry are estimated to be 0.10 Mg (0.10 tons); see Appendix A for details.

### 7.3 CARBON BLACK PRODUCTION

Carbon black is produced by pyrolyzing petrochemical oil feedstock. A compilation of facilities, locations, types of processes, and annual capacities is presented in Table 7-2. A description of the process used to manufacture carbon black and the emissions resulting from the various operations is presented below.

#### 7.3.1 Process Description

Carbon black is produced by partial combustion of hydrocarbons. The most common production process (which accounts for more than 98 percent of carbon black produced) is based on a feedstock consisting of a highly aromatic petrochemical or carbo chemical heavy oil.<sup>104</sup> Mercury can be expected to be present in the feedstock. Although the mercury content in the feedstock used to manufacture carbon black is not known, mercury content in petroleum crude is reported to range between 0.023 and 30 ppm by weight.<sup>105</sup> Figure 7-3 contains a flow diagram of this process.

Three primary raw materials are used in this process: preheated feedstock (either the petrochemical oil or carbochemical oil), which is preheated to a temperature between 150 and 250°C (302 and 482°F); preheated air; and an auxiliary fuel such as natural gas. The preheated oil and air are introduced into a furnace, or reactor, that is fired with the auxiliary fuel. A turbulent, high-temperature zone is created in the reactor by combusting the auxiliary fuel, and the preheated oil feedstock is introduced in this zone as an atomized spray. In this zone of the reactor, most of the oxygen is used to burn the auxiliary fuel, resulting in insufficient oxygen to combust the oil feedstock. Thus, pyrolysis (partial combustion) of the feedstock is achieved, and carbon black is produced. Most of the mercury in the feedstock is emitted in the hot exhaust gas from the reactor.

The product stream from the reactor is quenched with water, and any residual heat in the product stream is used to preheat the oil feedstock and combustion air before recovering the carbon in a fabric filter. Carbon recovered in the fabric filter is in a fluffy form. The fluffy carbon black may be ground in a grinder, if desired. Depending on the end use, carbon black may be shipped in a fluffy form or in the form of pellets. Pelletizing is done by a wet process in which carbon black is mixed with water along with a binder and fed into a pelletizer. The pellets are subsequently dried and bagged prior to shipping.

#### 7.3.2 Emission Control Measures

High-performance fabric filters are used to control PM emissions from main process streams during the manufacture of carbon black.<sup>104</sup> It is reported that the fabric filters can reduce PM emissions to levels as low as 6 mg/m<sup>3</sup> (normal m<sup>3</sup>). Mercury emissions from the reactor are primarily in the vapor phase. These emissions will proceed through the main process streams to the fabric filters. If the mercury remains in the vapor phase, the mercury control efficiency of the fabric filters is expected to be low. If the product gas stream is cooled to below 170°C (325°F), the fabric filter may capture a significant fraction of the condensed mercury, thus providing a high degree of emission control.

#### 7.3.3 Emissions

The processing unit with the greatest potential to emit mercury is the reactor. Mercury emission sources are indicated in Figure 7-3 by solid circles. Mercury, which is present in the oil feedstock, can potentially be emitted during the pyrolysis step. However, no data are available on the performance of the fabric filter control systems for mercury emissions. The only available data are for emissions from the oil-furnace process. These data show mercury emissions of 0.15 g/Mg ( $3 \times 10^{-4}$  lb/ton) from the main process vent.<sup>106</sup> The source of these data could not be obtained to verify the validity of the emission factors. Because the factors are not verified, they should be used with extreme caution.

Total 1995 mercury emissions from this industry are estimated to be 0.25 Mg (0.28 tons); see Appendix A for details.

### 7.4 BYPRODUCT COKE PRODUCTION

Byproduct coke, also called metallurgical coke, is a primary feedstock for the integrated iron and steel industry. Byproduct coke is so named because it is produced as a byproduct when coal is heated in an

TABLE 7-2. CARBON BLACK PRODUCTION FACILITIES

Company	Location	Type of process <sup>a</sup>	Annual capacity <sup>b</sup>	
			10 <sup>3</sup>	10 <sup>6</sup> lb
Cabot Corporation North American Carbon Black Division	Franklin, Louisiana	F	161	355
	Pampa, Texas	F	29	65
	Villa Platte, Louisiana	F	100	220
	Waverly, West Virginia	F	91	200
Chevron Chemical Company Olevins and Derivatives Division	Cedar Bayou, Texas	A	9	20
Columbian Chemicals Company	El Dorado, Arkansas	F	57	125
	Moundsville, West Virginia	F	88	195
	North Bend, Louisiana	F	100	220
	Ulysses, Kansas	F	36	80
Continental Carbon Company	Phenix City, Alabama	F	36	80
	Ponca City, Oklahoma	F	120	265
	Sunray, Texas	F	59	130
Degussa Corporation Pigment Group	Aransas Pass, Texas	F	54	120
	Belpre, Ohio	F	54	120
	New Iberia, Louisiana	F	109	240
Ebonex Corporation	Melvindale, Michigan	C	4	8
Engineered Carbons, Inc.	Baytown, Texas	F	86	190
	Borger, Texas	F and T	102	225
	Orange, Texas	F	61	135
General Carbon Company	Los Angeles, California	C	0.5	1
Hoover Color Corporation	Hiwassee, Virginia	C	0.5	1
Sir Richardson Carbon Company	Addis, Louisiana	F	120	265
	Big Spring, Texas	F	54	120
	Borger, Texas	F	129	285
TOTAL			1,660	3,665

Source: Reference 11.

<sup>a</sup>A = acetylene decomposition

C = combustion

F = furnace

T = thermal

<sup>b</sup>Capacities are variable and based on SRI estimates as of January 1, 1996.

Figure 7-3. Process flow diagram for carbon black manufacturing process.<sup>104</sup>

oxygen-free atmosphere (coked) to remove the volatile components of the coal. The material remaining is a carbon mass called coke. The volatile components are refined to produce clean coke-oven gas, tar, sulfur, ammonium sulfate, and light oil.<sup>107</sup> Table 7-3 contains a list of byproduct coke oven facilities reported to be in operation in 1991.<sup>108</sup> A description of the process used to manufacture byproduct coke and the emissions resulting from the various operations is presented below.

#### 7.4.1 Process Description

Coke is currently produced in two types of coke oven batteries: the slot oven byproduct battery and the nonrecovery battery. The slot oven byproduct type is the most commonly used battery; over 99 percent of coke produced in 1990 was produced in this type of battery. The nonrecovery battery, as the name suggests, is one where the products of distillation are not recovered and are immediately combusted to provide energy within the plant. The nonrecovery battery is currently used at only one location; however, it is expected to be a more popular choice when existing plants are reconstructed. Figures 7-4 and 7-5 present the general layout and the emission points of a typical byproduct coke oven battery.

The byproduct coke oven battery consists of 20 to 100 adjacent ovens with common side walls that are made of high quality silica and other types of refractory brick. Typically, the individual slot ovens are 11 to 16.8 m (36 to 55 ft) long, 0.35 to 0.5 m (1.1 to 1.6 ft) wide, and 3.0 to 6.7 m (9.8 to 22 ft) high. The wall separating adjacent ovens, as well as each end wall, is made of a series of heating flues.<sup>107</sup> Depending on the dimensions, the production capacity may range from 6.8 to 35 Mg (7.5 to 39 tons) of coke per batch.

Pulverized coal, which is the feedstock, is fed through ports located on the top of each oven by a car (referred to as a larry car) that travels on tracks along the top of each battery. After the oven is charged with coal, the ports are sealed ("luted") with a wet clay mixture, and gaseous fuel (usually clean coke oven gas) is combusted in the flues located between the ovens to provide the energy for the pyrolysis.<sup>107</sup>

The operation of each oven is cyclic, but the battery contains a sufficiently large number of ovens to produce an essentially continuous flow of raw coke oven gas. The individual ovens are charged and emptied at approximately equal time intervals during the coking cycle. The coking process takes between 15 and 30 hours, at the end of which almost all the volatile matter from the coal is driven off, thus forming coke. The coking time is determined by the coal mixture, moisture content, rate of underfiring, and the desired properties of the coke. When demand for coke is low, coking times can be extended to 24 to 48 hours. Coking temperatures generally range from 900° to 1,000°C (1,650° to 2,000°F). The gases that evolve during the thermal distillation are removed through the offtake system and sent to the byproduct plant for recovery.<sup>107</sup>

At the end of the coking cycle, doors on both ends of the oven are removed and the incandescent coke is pushed from the oven by a ram that is extended from the pusher machine. The coke is pushed through a coke guide into a special railroad car called a quench car. The quench car carries the coke to a quench tower where it is deluged with water to prevent the coke from burning after exposure to air. The quenched coke is discharged onto an inclined coke wharf to allow the excess water to drain and to cool the coke to a reasonable handling temperature. The coke is then crushed and screened to the proper size for the blast furnace operation.<sup>107</sup>

The mercury content in coal was presented in Section 6.1. Table 6-4 presented data pertaining to mercury levels in various types of U.S. coals. Depending on the type of coal used, the mercury content can be as high as 8 ppm by weight; however, values of about 1 ppm are more typical. Consequently, the gases that evolve from the coking operation are likely to contain mercury.<sup>110</sup>

#### 7.4.2 Emission Control Measures

Emissions from charging coal into the ovens are controlled by stage charging in which coal is discharged from the larry car hoppers in an ordered sequence that maintains an open tunnel head at the top of the oven to provide an exit space for the gas until the last hopper is emptied. An important aspect of stage charging is adequate aspiration, which is used to pull the gas generated during charging from the ovens into the regular gas handling equipment.<sup>107</sup>

TABLE 7-3. BYPRODUCT COKE PRODUCERS IN THE UNITED STATES IN 1991

Facility	No. of batteries	Total No. of ovens	Total capacity, tons/d
Acme Steel, Chicago, IL	2	100	1,600
Armco, Inc., Ashland, KY	2	146	2,700
Armco, Inc., Middleton, OH	3	203	4,535
Bethlehem Steel, Bethlehem, PA	3	284	3,944
Bethlehem Steel, Burns Harbor, IN	2	164	4,380
Bethlehem Steel, Lackawanna, NY	2	152	1,872
Bethlehem Steel, Sparrows Point, MD	3	210	4,069
Geneva Steel, Orem, UT	1	208	2,250
Gulf States Steel, Gadsden, AL	2	130	2,800
Inland Steel, East Chicago, IN	6	446	5,775
LTV Steel, Pittsburgh, PA	5	315	5,404
LTV Steel, Chicago, IL	1	60	1,600
LTV Steel, Cleveland, OH	2	126	3,200
LTV Steel, Warren, OH	1	85	1,500
National Steel, Granite City, IL	2	90	1,520
National Steel, Ecorse, MI	1	78	925
USS, Div. of USX Corp., Clairton, PM	12	816	12,640
USS, Div. of USX Corp., Gary, IN	6	422	7,135
Wheeling-Pittsburgh Steel, East Steubenville, WV	4	224	3,800
Total	58	4,259	71,649

Source: Reference 108.

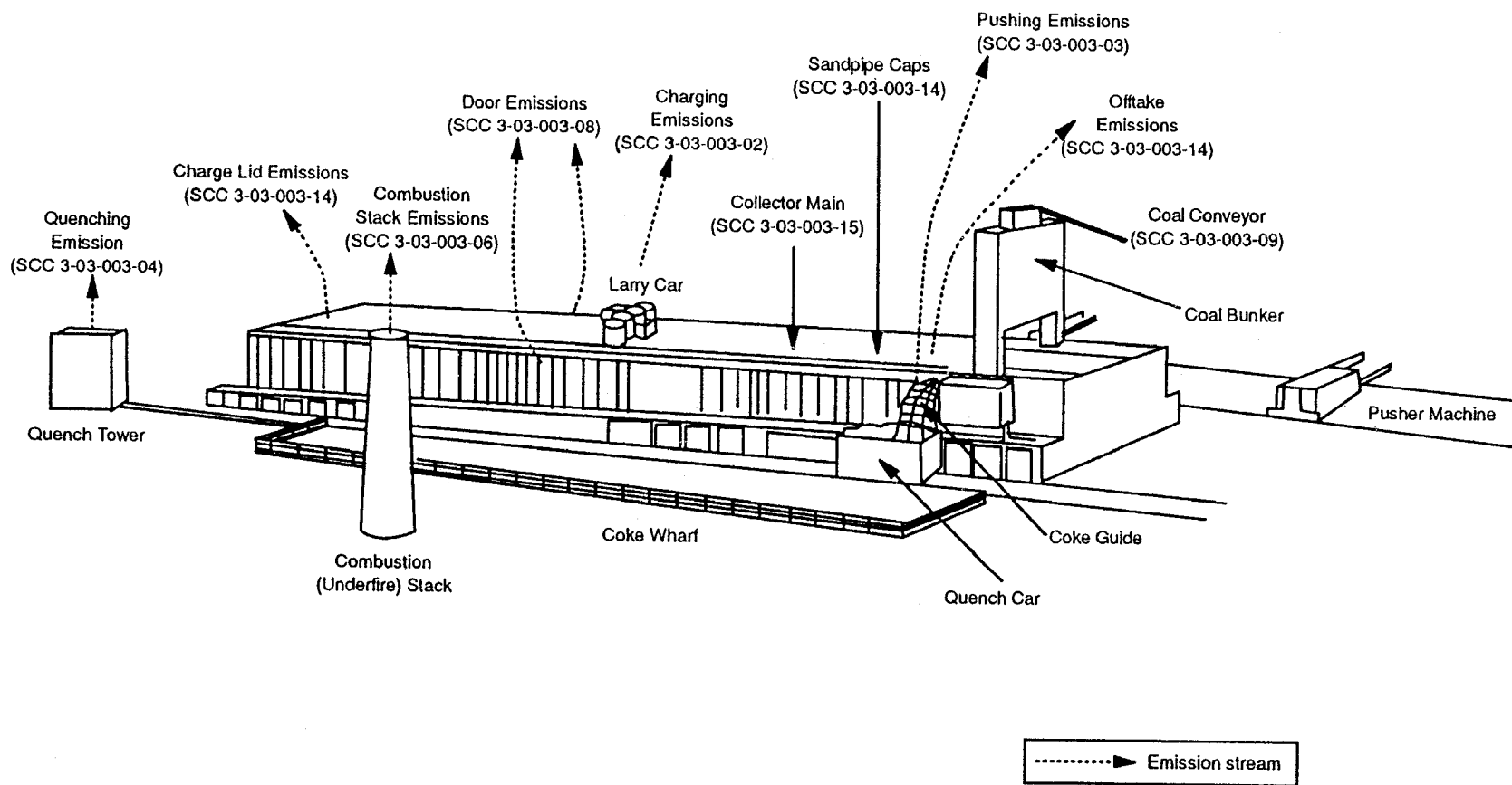


Figure 7-4. Schematic of byproduct coke oven battery.<sup>107</sup>



**TYPES OF AIR POLLUTION EMISSIONS  
FROM COKE OVEN BATTERIES**

- ① Pushing emissions
- ② Charging emissions
- ③ Door emissions
- ④ Topside emissions
- ⑤ Battery underfire emissions

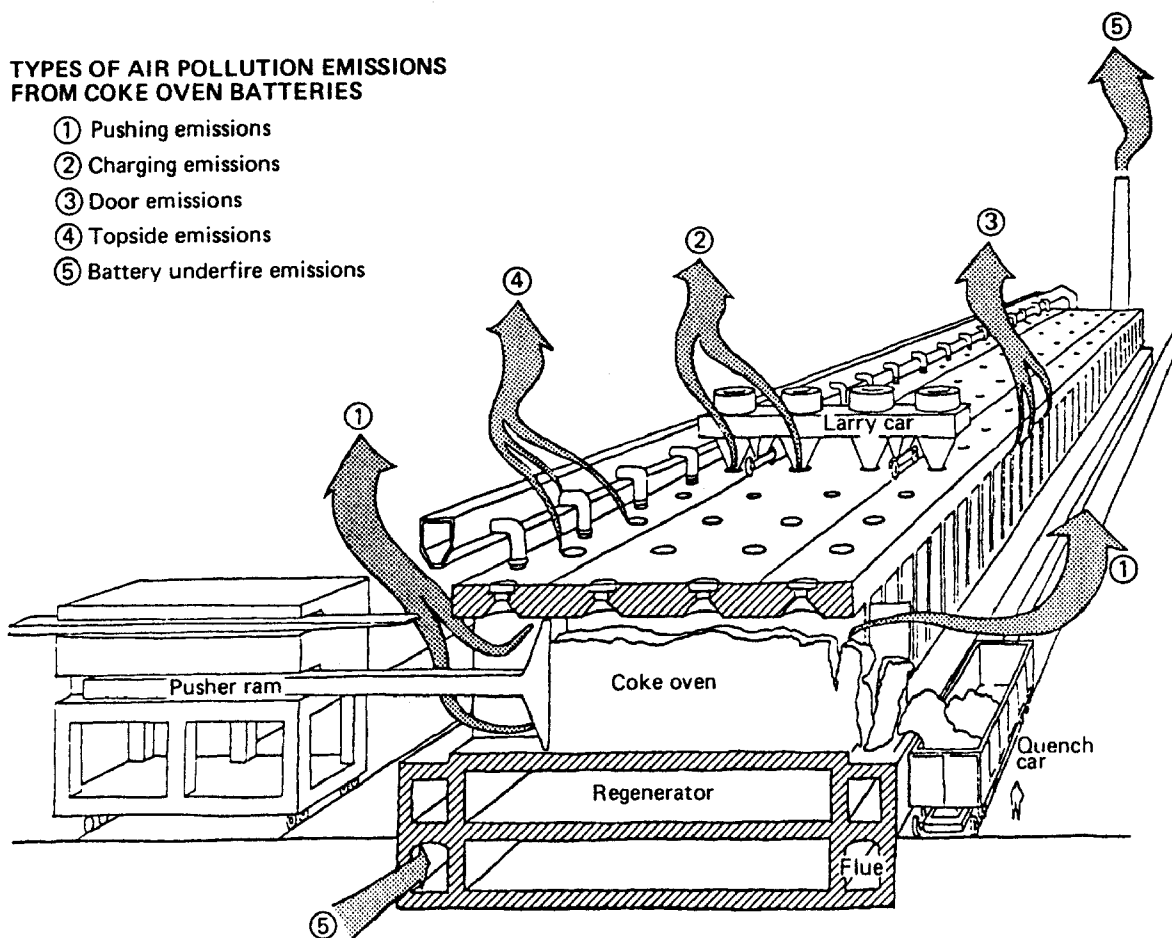


Figure 7-5. Types of air pollution emissions from coke oven batteries.<sup>109</sup>

During the coking cycle, pollutants are emitted from leaks on the battery, including leaks from doors, from lids that cover the charging ports, and from the offtake system. Because the oven is maintained under a positive pressure, these leaks occur from small openings, such as gaps where metal seals mate against some other part of the oven. Small gaps seal by the condensation of tar. Door leaks on most batteries are controlled by repairing and maintaining doors, door seals, and jambs to prevent large gaps between the metal seal and the jamb. The manual application of a supplemental sealant such as sodium silicate is used at some plants to further reduce door leaks. A few batteries control door leaks by the external application of a luting material to provide a seal (called hand-luted doors). Lid leaks and offtake leaks are controlled by applying luting material around sealing edges to stop leaks and reluting when leaks are observed. The control of leaks requires a diligent work practice program that includes locating leaks and then identifying and correcting their cause.<sup>107</sup>

Pushing coke into the quench car is a significant source of PM emissions. Most facilities control pushing emissions by using mobile scrubber cars with hoods, shed enclosures evacuated to a gas cleaning device, or traveling hoods with a fixed duct leading to a stationary gas cleaner. Emission control devices used to control emissions from quenching include ESP's, fabric filters, and wet scrubbers. These control devices are effective primarily for PM control. No data are available on the performance of these systems for control of mercury emissions. However, because these devices typically operate at elevated temperatures ( $>170^{\circ}\text{C}$  [ $>325^{\circ}\text{F}$ ]), mercury removal is anticipated to be limited.

Fugitive particulate matter emissions are generated from material handling operations such as unloading, storing, and grinding of coal; as well as screening, crushing, storing, and loading of coke. These coal and coke handling PM emissions may be controlled by the use of cyclones.<sup>107</sup>

#### 7.4.3 Emissions

Mercury emissions can be generated in small quantities during coal preparation and handling as fugitive particulate matter because mercury is present as a trace contaminant in coal. Mercury also may be volatilized and released during charging and pushing operations. During the coking cycle, mercury may be volatilized and released to the atmosphere through poorly sealed doors, charge lids, and offtake caps, and through cracks which may develop in oven brickwork, the offtakes, and collector mains.

There are no mercury emission data for byproduct coke ovens in the U.S. However, emission factors used in Germany for coke production range from 0.01 to 0.03 g/Mg ( $2 \times 10^{-5}$  to  $6 \times 10^{-5}$  lb/ton) of coke produced.<sup>33</sup> It is important to note that U.S. coke producers use a high quality cleaned coal while their European counterparts do not. If it is assumed that the coal cleaning process results in a 20 percent reduction in mercury emissions (see Section 6.1.4.1), then the resultant U.S. mercury emission factor for coke production would be 0.025 g/Mg ( $5 \times 10^{-5}$  lb/ton).

Total 1991 mercury emissions from this industry are estimated to be 0.59 Mg (0.65 tons); see Appendix A for details.

### 7.5 PRIMARY LEAD SMELTING

Lead is recovered from a sulfide ore, primarily galena (lead sulfide--PbS), which also contains small amounts of copper, iron, zinc, and other trace elements such as mercury. In 1994, the production of refined primary lead from domestic ores and base bullion was 328,000 Mg (361,500 tons), which represents an increase of about 6 percent over 1993 production.<sup>111</sup> A list of primary lead smelters currently in operation within the United States is given in Table 7-4.<sup>111</sup> A description of the process used to manufacture lead and the emissions resulting from the various operations are presented below.

TABLE 7-4. DOMESTIC PRIMARY LEAD SMELTERS AND REFINERIES

Smelter	Refinery	Estimated refinery capacity, Mg (tons)
ASARCO, East Helena, MT	ASARCO, Omaha, NE <sup>a</sup>	60,000 (66,100)
ASARCO, Glover, MO	Same site	125,000 (137,800)
Doe Run, Herculaneum, MO	Same site	200,000 (220,400)

Source: Reference 111.

<sup>a</sup>Closed permanently for lead refining as of May 31, 1996. There is limited refinery capacity at East Helena, MT.

#### 7.5.1 Process Description

Lead ores are concentrated at or near the mine and shipped to the smelter as the ore concentrate. Figure 7-6 contains a process flow diagram of primary lead smelting. The recovery of lead from the lead ore consists of three main steps: sintering, reduction, and refining.<sup>112</sup>

Sintering occurs in a sintering machine, which is essentially a large oven containing a continuous steel pallet conveyor belt. Each pallet consists of perforated grates, beneath which are wind boxes connected to fans to provide excess air through the moving sinter charge. The sintering reactions take place at about 1000°C (1832°F) during which lead sulfide is oxidized to lead oxide. The gas from the front end of the sintering machine, containing 2.5 to 5 percent SO<sub>2</sub>, is vented to gas cleaning equipment before being sent to a sulfuric acid plant. Gases from the rear of the sinter machine are recirculated through the moving grate and then, typically, vented to a baghouse. The desulfurized sinter roast is crushed and then transported to the blast furnace in charge cars. Since mercury and its compounds vaporize below the sintering temperature, most of the mercury present in the ore can be expected to be emitted during sintering either as elemental mercury or as mercuric oxide.

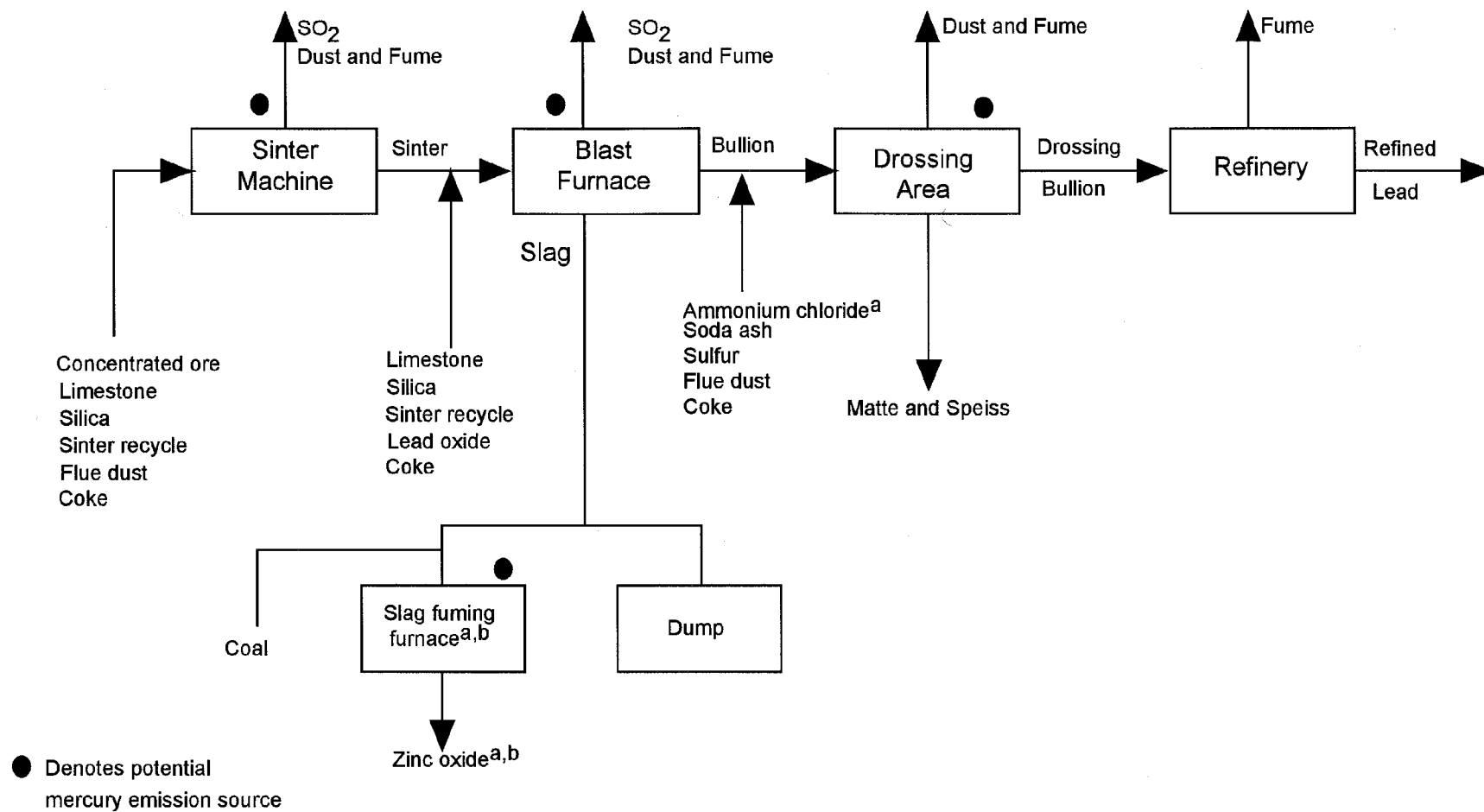
Reduction of the sintered lead is carried out in a blast furnace at a temperature of 1600°C (2920°F). The furnace is charged with a mixture of sinter (80 to 90 percent of charge), metallurgical coke (8 to 14 percent of charge), and other materials, such as limestone, silica, litharge, and other constituents, which are balanced to form a fluid slag. In the blast furnace, the charge descends through the furnace shaft into the smelting zone, where it becomes molten, and then into a series of settlers that allow the slag to separate from the lead. The slag is cooled and sent to storage; the molten lead, about 85 percent pure, is transported in pots to the dross area for refining. Any residual mercury remaining in the roast from the sintering operation is expected to be released during this reduction process.

The drossing area consists of a variety of interconnected kettles heated by natural gas. The lead pots from the blast furnace are poured into receiving kettles and cooled. The copper dross rises to the top and can be skimmed off for processing. The remaining lead dross is transferred to a finishing kettle where other materials are added to facilitate further separation of impurities. In the finishing kettles, the lead dross bullion settles to the bottom, is removed, and sent to the refinery. The matte and speiss rise to the top, are removed, and sent to copper smelters.

Further refining of the lead bullion is carried out in cast iron kettles. Refined lead, which is 99.99 to 99.999 percent pure, is cast into pigs for shipment.

#### 7.5.2 Emission Control Measures

Emission controls on lead smelter operations are employed for controlling PM and SO<sub>2</sub> emissions resulting from the blast furnace and sintering machines. Centrifugal collectors (cyclones) may be used in conjunction with fabric filters or ESP's for PM control. The blast furnace and the sintering machine operate at very high temperatures (in excess of 1000°C [1832°F]); as a result, mercury is emitted from these sources in vapor form. Therefore, particulate control devices would have little effect on mercury



<sup>a</sup>Not at ASARCO, East Helena, Montana.

<sup>b</sup>Not at ASARCO, Glover, Missouri.

Figure 7-6. Typical primary lead processing scheme.<sup>112</sup>

emissions from the sintering machine and blast furnace. However, no collection efficiency data are available for mercury using these systems.

Control of SO<sub>2</sub> emissions is achieved by absorption to form sulfuric acid in the sulfuric acid plants, which are commonly part of lead smelting plants.

### 7.5.3 Emissions

Mercury, which may be present in the ore, may be emitted during the sintering and blast furnace steps and, to a lesser extent, in the dressing area because these processes take place at high temperatures. None of the primary lead smelters crush the ore at the smelter; all ore crushing and concentration is performed at or near the mine. The smelters receive the ore concentrate for processing. Mercury emission sources are indicated on Figure 7-6 by solid circles.

The available emission factor data for mercury emissions from primary lead smelting are for a custom smelter operated by ASARCO in El Paso, Texas; this facility ceased operating in 1985. No recent mercury emission factors are available for the three current primary lead smelters. The custom smelter in El Paso obtained lead ore from several sources both within and outside the United States. These ores had a variable mercury content depending upon the source of the ore. Two of the three current smelters are not custom smelters; they typically process ore from the vicinity of the smelter. The two smelters in Missouri use ore only from southeast Missouri; these ores have a very low mercury content. These two smelters combined have over 84 percent of the total U.S. smelter capacity. The ASARCO-East Helena plant, although a custom smelter, generally also processes low mercury concentrates. None of the three primary lead smelters reported mercury emission data in the 1994 TRI.

Because the El Paso facility data were based on ores with a variable mercury content, and the current major sources of lead ore have a very low mercury content, use of those emission factors will lead to an overestimation of current emissions. A better estimating method would be to use the actual mercury content of the ore and estimate emissions based on those data. The major domestic source of lead ore concentrate is from the southeast Missouri area near the Glover and Herculaneum smelters. Data on mercury content in lead concentrates from this area indicate the mercury concentration to be less than 0.2 parts per million (ppm).<sup>113</sup> Using a mercury concentration of 0.2 ppm and particulate matter (PM) emission factors from the EPA AP-42 section on primary lead smelting, the upper limit for mercury emissions is estimated to be 0.10 Mg (0.11 tons); see Appendix A for estimation procedures.<sup>112</sup>

## 7.6 PRIMARY COPPER SMELTING

Copper is recovered from a sulfide ore principally by pyrometallurgical smelting methods. Copper ores contain small quantities of arsenic, cadmium, lead, antimony, and other heavy metals including mercury. Data pertaining to mercury content in the ore are not available.

A list of primary copper smelters currently in operation within the U.S. is given in Table 7-5. In 1995, the total U.S. capacity for the eight primary copper smelters was 1,413,000 Mg (1,557,000 tons). The total capacity in 1996 decreased to 1,354,000 Mg (1,492,000 tons) due to the closure of the Copper Range smelter.<sup>114</sup> In 1996, there were 19 refineries for primary copper processing; five used an electrolytic process and 14 used an electrowinning process. In addition, there were seven refineries for secondary copper processing.<sup>114</sup> Since the mercury levels in the copper from the smelter would be very low, the mercury emissions from the refining process are expected to be very small. Therefore, no tabulation of the individual refineries is presented.

A description of the process used to manufacture copper and the emissions resulting from the various operations is presented below.<sup>115</sup>

### 7.6.1 Process Description

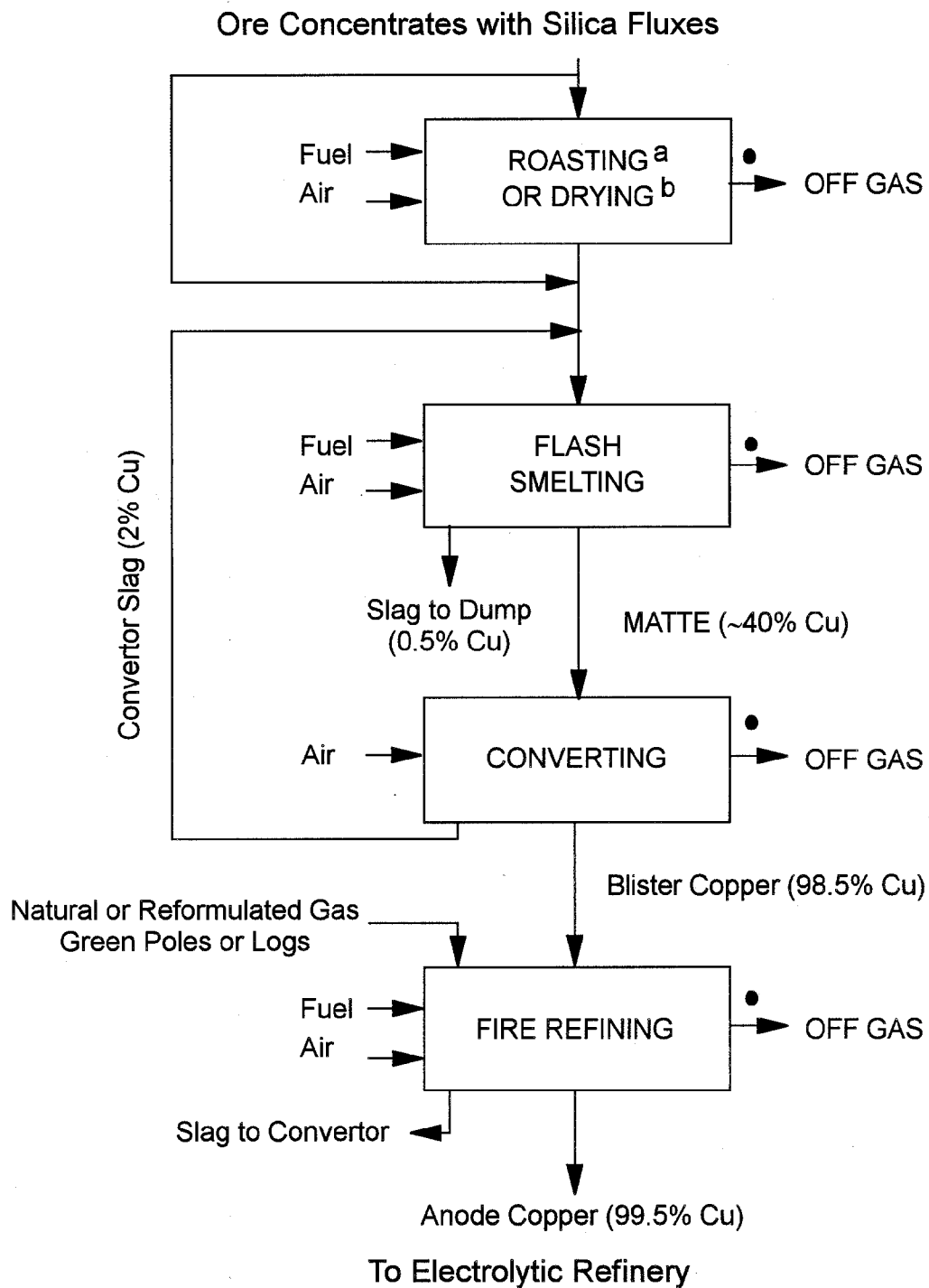
The pyrometallurgical copper smelting process is illustrated in Figure 7-7.<sup>115</sup> The traditionally used process includes roasting of ore concentrates to produce calcine, smelting of roasted (calcine feed) or unroasted (green feed) ore concentrates to produce matte, and converting of the matte to yield blister

TABLE 7-5. U.S. PRIMARY COPPER SMELTERS

Company	Location	Process	Capacity, 10 <sup>3</sup> Mg (10 <sup>3</sup> tons)	
			1995	1996
ASARCO, Inc.	El Paso, TX Hayden, AZ	ConTop flash furnace Inco flash	91 (100) 172 (190)	100 (110) 172 (190)
Copper Range Company <sup>a</sup>	White Pine, MI	Reverberatory	68 (75)	0 (0)
Cypruss Climax Metals Company	Globe, AZ	Isasmelt/Electric	163 (180)	163 (180)
Kennecott	Garfield, UT	Outokumpu	256 (282)	256 (282)
Magma Copper Company	San Manuel, AZ	Outokumpu flash	309 (340)	309 (340)
Phelps Dodge Corp.	Hildalgo, NM Hurley, NM	Outokumpu flash Inco flash	200 (220) 154 (170)	200 (220) 154 (170)
		Total	1,413 (1,557)	1,354 (1,492)

Source: Reference 114.

<sup>a</sup>Closed in February 1995.



• Denotes potential mercury emission source

<sup>a</sup>First step in the traditionally used copper-smelting process.

<sup>b</sup>First step in the currently used copper-smelting process.

Figure 7-7. Typical primary copper smelter process.<sup>115</sup>

copper product (about 99 percent pure). Typically, the blister copper is fire refined in an anode furnace, cast into "anodes" and sent to an electrolytic refinery for further impurity elimination. Copper smelters currently process ore concentrates by drying them in fluidized bed dryers and then converting and refining the dried product in the same manner as the traditionally used process.<sup>115</sup>

In roasting, charge material of copper concentrate mixed with a siliceous flux (often a low grade ore) is heated in air to about 650°C (1200°F), eliminating 20 to 50 percent of the sulfur as SO<sub>2</sub>. Portions of such impurities as antimony, arsenic, and lead are driven off, and some iron is converted to oxide. The roasted product, calcine, serves as a dried and heated charge for the smelting furnace. Either multiple hearth or fluidized bed roasters are used for roasting copper concentrate. Multiple hearth roasters accept moist concentrate, whereas fluid bed roasters are fed finely ground material (60 percent minus 200 mesh). With both of these types, the roasting is autogenous. Because there is less air dilution, higher SO<sub>2</sub> concentrations are present in fluidized bed roaster gases than in multiple hearth roaster gases. Because mercury has a boiling point of 350°C (660°F), most of the mercury in the ore may be emitted during roasting.

In the smelting process, either hot calcines from the roaster or raw unroasted or dried concentrate is melted with siliceous flux in a flash smelting furnace to produce copper matte, a molten mixture of cuprous sulfide (Cu<sub>2</sub>S), ferrous sulfide (FeS), and some heavy metals. The required heat comes from partial oxidation of the sulfide charge and from burning external fuel. Most of the iron and some of the impurities in the charge oxidize with the fluxes to form a slag atop the molten bath, which is periodically removed and discarded. Copper matte remains in the furnace until tapped. Mattes produced by the domestic industry range from 35 to 65 percent copper, with 45 percent the most common. The copper content percentage is referred to as the matte grade. Currently, four smelting furnace technologies are used in the United States: electric, ConTop (flash) Outokumpu (flash), and Inco (flash). There are no reverberatory furnaces currently in operation in the U.S. Flash furnaces may operate at temperatures as high as 1200 to 1300°C (2190 to 2370°F). Even though the exact temperatures at which the other furnace technology (electric) operates is not known, it is probable that it operates at temperatures higher than the boiling point of mercury. Therefore, any residual mercury that remains in the calcine may be emitted during the smelting step.

For smelting in electric arc furnaces, heat is generated by the flow of an electric current in carbon electrodes lowered through the furnace roof and submerged in the slag layer of the molten bath. The feed generally consists of dried concentrates or calcines, and charging wet concentrates is avoided. The matte is periodically tapped and the slag is skimmed at frequent intervals. Electric furnaces do not produce fuel combustion gases, so effluent gas flow rates are low and SO<sub>2</sub> concentrations are high.

Flash furnace smelting combines the operations of roasting and smelting to produce a high grade copper matte from concentrates and flux. In flash smelting, dried ore concentrates and finely ground fluxes are injected, together with oxygen, preheated air, or a mixture of both, into a furnace of special design, where temperature is maintained at approximately 1200 to 1300°C (2190 to 2370°F). Most flash furnaces, in contrast to reverberatory and electric furnaces, use the heat generated from partial oxidation of their sulfide charge to provide much or all of the energy (heat) required for smelting. They also produce offgas streams containing high concentrations of SO<sub>2</sub>. Other flash furnaces, such as ConTop cyclone reactors, use oxyfuel combustion to generate the heat required for oxidation.

Slag produced by flash furnace operations typically contains higher amounts of copper than does that from electric furnace operations. As a result, the flash furnace and converter slags are treated in a slag cleaning furnace to recover the copper (not conducted at the ASARCO, Hayden facility). Slag cleaning furnaces usually are small electric furnaces. The flash furnace and converter slags are charged to a slag cleaning furnace and are allowed to settle under reducing conditions, with the addition of coke or iron sulfide. The copper, which is in oxide form in the slag, is converted to copper sulfide, is subsequently removed from the furnace and is charged to a converter with regular matte. If the slag's copper content is low, the slag is discarded.

The final step in the production of blister copper is converting, with the purposes of eliminating the remaining iron and sulfur present in the matte and leaving molten "blister" copper. All but one U. S. smelter uses Pierce-Smith converters, which are refractory lined cylindrical steel shells mounted on trunnions at one end, and rotated about the major axis for charging and pouring. An opening in the center of the converter functions as a mouth through which molten matte, siliceous flux, and scrap copper are charged and gaseous products are vented. Air or oxygen-rich air is blown through the molten matte. Iron sulfide (FeS) is oxidized to iron oxide (FeO) and SO<sub>2</sub>, and the FeO blowing and slag skimming are repeated until an adequate amount of relatively pure Cu<sub>2</sub>S, called "white metal", accumulates in the bottom of the converter. A renewed air blast



oxidizes the copper sulfide to SO<sub>2</sub>, leaving blister copper in the converter. The blister copper is subsequently removed and transferred to refining facilities. This segment of converter operation is termed the finish blow. The SO<sub>2</sub> produced throughout the operation is vented to pollution control devices.

One domestic smelter uses Hoboken converters. The Hoboken converter is essentially like a conventional Pierce-Smith converter, except that this vessel is fitted with a side flue at one end shaped as an inverted U. This flue arrangement permits siphoning of gases from the interior of the converter directly to the offgas collection system, leaving the converter mouth under a slight vacuum. The Hoboken converters are also equipped with secondary hoods to further control emissions.

Blister copper usually contains from 98.5 to 99.5 percent pure copper. Impurities may include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, and zinc. To purify blister copper further, fire refining and electrolytic refining are used. In fire refining, blister copper is placed in an anode furnace, a flux is usually added, and air is blown through the molten mixture to oxidize remaining impurities, which are removed as a slag. The remaining metal bath is subjected to a reducing atmosphere to reconvert cuprous oxide to copper. Temperature in the furnace is around 1100°C (2010°F). The fire-refined copper is cast into anodes. Further refining separates the copper from impurities by electrolysis in a solution containing copper sulfate and sulfuric acid. Metallic impurities precipitate from the solution and form a sludge that is removed and treated to recover precious metals. Copper is dissolved from the anode and deposited at the cathode. Cathode copper is remelted and cast into bars, rods, ingots, or slabs for marketing purposes. The copper produced is 99.95 to 99.97 percent pure. Any mercury emissions during the refining step will only be minimal.

#### 7.6.2 Emission Control Measures

Emission controls on copper smelters are employed for controlling PM and SO<sub>2</sub> emissions resulting from roasters, smelting furnaces, and converters. Electrostatic precipitators are the most common PM control devices employed at copper smelting facilities. Control of SO<sub>2</sub> emissions is achieved by absorption to sulfuric acid in the sulfuric acid plants, which are commonly part of all copper smelting plants.<sup>115</sup>

#### 7.6.3 Emissions

The main source of mercury will be during the roasting step and in the smelting furnace. Converters and refining furnaces may emit any residual mercury left in the calcine. These sources are denoted by solid circles in Figure 7-7.

In 1993, the Emission Standards Division of the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, issued an information collection request to all eight of the primary copper smelters operating at that time for data on mercury emissions. The reported values represented annualized mercury emissions, in pounds per year (lb/yr), from both stack and fugitive emission points at each smelter. With the exclusion of Copper Range, which is closed, the self-reported values for mercury emissions in 1993 ranged from 0 to 35 lb/yr and the total for all smelters was 55.0 kg/yr (121.2 lb/yr) or 0.055 Mg (0.061 tons/yr).<sup>116</sup> In 1994, smelter production from domestic and foreign ores increased about 3.15 percent over 1993 production.<sup>114</sup>

Total 1994 mercury emissions from this industry are estimated to be 0.057 Mg (0.063 tons); see Appendix A for details.

### 7.7 PETROLEUM REFINING

**[This section is a condensation of the petroleum refining section in the 1993 Mercury L&E document; except for plant location information, no new data have been added.]**

Petroleum refining involves the conversion of crude petroleum oil into refined products, including liquified petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petroleum industry.

As of January 1995, there were 34 oil companies in the United States with operable atmospheric crude oil distillation capacities in excess of 100,000 barrels per calendar day. These oil companies operated refineries at a total of 107 different locations. In addition, there were 53 companies with distillation

capacities of less than 100,000 barrels per calendar day. A listing of all companies, specific refinery locations, and distillation capacities is presented in Appendix D.<sup>117</sup>

Mercury is reported to be present in petroleum crude, and its content in petroleum crude is reported to range between 0.023 and 30 ppm by weight.<sup>105</sup> A description of the processes used in petroleum refining and emissions resulting from the various operations is presented below.

#### 7.7.1 Process Description

Petroleum refining is a very complex and highly integrated process. This process description represents a general petroleum refining operation and highlights only the common process components. Actual processes may vary among refineries depending upon the specific products produced. The operations at petroleum refineries are classified into five general categories, as listed below:<sup>118,119</sup>

1. Separation processes,
2. Petroleum conversion processes,
3. Petroleum treating processes,
4. Feedstock and product handling, and
5. Auxiliary facilities.

7.7.1.1 Separation Processes. Constituents of crude oil include paraffinic, naphthenic, and aromatic hydrocarbon compounds; impurities include sulfur, nitrogen, and metals. Three separation processes used to separate these constituents include: atmospheric distillation, vacuum distillation, and recovery of light ends (gas processing).

Atmospheric distillation results in the formation of bottoms consisting of high-boiling-point hydrocarbons. Topped crude withdrawn from the bottoms of atmospheric distillation can be separated further by vacuum distillation.

In vacuum distillation, the topped crude is heated in a process heater to temperatures ranging from 370° to 425°C (700° to 800°F) and subsequently flashed in a multi-tray vacuum distillation column, operating at vacuums ranging from 350 to 1,400 kg/m<sup>2</sup> (0.5 to 2.0 psia). Standard petroleum fractions withdrawn from the vacuum distillation include lube distillates, vacuum oil, asphalt stocks, and residual oils. Distillation is carried out at temperatures higher than the boiling point of mercury and can be expected to be the primary source of mercury emissions.

7.7.1.2 Conversion Processes. Conversion processes include (1) cracking, coking, and visbreaking, which break large molecules into smaller molecules; (2) isomerization and reforming processes to rearrange the structures of molecules; and (3) polymerization and alkylation to combine small molecules into larger ones. Residual mercury from the separation processes is probably emitted during the conversion processes.

Catalytic cracking uses heat, pressure, and catalysts to convert heavy oils into lighter products. Feedstocks are usually gas oils from atmospheric distillation, vacuum distillation, coking, and deasphalting processes, with a boiling range of 340° to 540°C (650° to 1000°F). Two types of cracking units, the fluidized catalytic cracking (FCC) unit and the moving-bed catalytic cracking unit, are used in the refineries.

Visbreaking is a thermal cracking process used to reduce the viscosity of the topped crude or vacuum distillation residues. The feedstock is heated and thermally cracked at a temperature ranging between 455° and 480°C (850° and 900°F) and pressure ranging between 3.5 and 17.6 kg/cm<sup>2</sup> (50 and 250 psia). The cracked products are quenched with gas oil and flashed into a fractionator. The vapor overhead from the fractionator is separated into light distillate products. A heavy distillate is recovered from the fractionator liquid.

Coking is also a thermal cracking process used to convert low value residual fuel oil to higher value gas oil and petroleum coke. It is carried out at high temperature and low pressure, and the resulting products include petroleum coke, gas oils, and lighter petroleum stocks.

The conversion steps, cracking, coking, and visbreaking, described above can be expected to be secondary sources of mercury emissions.

Equipment commonly used during conversion includes process heaters and reformers. Process heaters are used to raise the temperature of petroleum feedstocks to a maximum of 510°C (950°F). Fuels burned include refinery gas, natural gas, residual fuel oils, or combinations. Reformers are reactors where the heat for the reaction is supplied by burning fuel.

7.7.1.3 Treatment Processes. Petroleum treatment processes include hydrodesulfurization, hydrotreating, chemical sweetening, acid gas removal, and deasphalting. These treatment methods are used to stabilize and upgrade petroleum products. Removal of undesirable elements, such as sulfur, nitrogen, and oxygen, is accomplished by hydrodesulfurization, hydrotreating, chemical sweetening, and acid gas removal. Deasphalting is carried out to separate asphaltic and resinous materials from petroleum products. Hydrotreating is a process in which the oil feed is treated by mixing with hydrogen in a fixed-bed catalyst reactor. Removal of acid gas involves controlling emissions of SO<sub>2</sub>. Elemental sulfur is recovered as a byproduct.

Any residual mercury left over in the feedstock after the separation and conversion steps can be expected to be emitted during the treatment step.

7.7.1.4 Feedstock and Product Handling. This includes storage, blending, loading, and unloading of petroleum crude and products. No mercury emissions are expected during these steps.

7.7.1.5 Auxiliary Facilities. Auxiliary facilities include boilers, gas turbines, wastewater treatment facilities, hydrogen plants, cooling towers, and sulfur recovery units. Boilers and gas turbines cogeneration units within petroleum refineries may burn refinery gas.

## 7.7.2 Emission Control Measures

Control of VOC (and in some instances, CO) emissions from distillation, catalytic cracking, coking, blowdown system, sweetening, and asphalt blowing is achieved by flares. In some instances, the VOC-laden gas stream is also used as fuel in process heaters.<sup>118</sup>

Control of PM emissions from catalytic cracking is achieved by using cyclones in conjunction with ESP's.

## 7.7.3 Emissions

Emissions of mercury can be expected during the process steps where petroleum crude is processed at high temperatures, such as the distillation, cracking, visbreaking, and other conversion steps. Other emissions from petroleum refining operations include mainly PM, VOC, and products of fuel combustion.<sup>118</sup> An emission factor for uncontrolled emissions from the fluid coking unit in the conversion step was cited in SPECIATE but the source of these data could not be obtained in order to verify the validity of the emission factors so the factor is not cited. The only other available data pertain to emissions from process heaters and reformers. Based on a series of emission tests carried out in California, emission estimates for mercury were presented for refinery gas-fired process heaters, boilers, gas turbine cogeneration units, and asphalt fume incinerators.<sup>120</sup> These sources are auxiliary equipment that use fuels from a combination of sources. These data are not representative of mercury emissions from the refining process.

## 7.8 MUNICIPAL SOLID WASTE LANDFILLS

A municipal solid waste (MSW) landfill is a discrete area of land or an excavation that receives household waste and is not a land application unit, surface impoundment, injection well, or waste pile. A MSW landfill may also receive other types of wastes, such as commercial solid waste, nonhazardous sludge, and industrial solid waste.<sup>121</sup>

Municipal solid waste management in the United States is dominated by disposal in landfills. In 1994, approximately 60 percent of municipal solid waste was landfilled, 16 percent was incinerated, and 24 percent was recycled or composted.<sup>68</sup> There were an estimated 3,600 active MSW landfills in the United States in 1996.<sup>122</sup> In 1994, active landfills received an estimated 115 million megagrams (Mg) (127 million tons) of MSW.<sup>68</sup>

### 7.8.1 Process Description

The three major design methods for MSW landfills are the area method, the trench method, and the ramp method. These methods use a three-step process that consists of spreading the waste, compacting the waste, and covering the waste with soil. The trench and ramp methods are not commonly used, particularly when liners and leachate collection systems are used. The area fill method involves placing waste on the ground surface or landfill liner, spreading it in layers, and compacting with heavy equipment. The trench method entails excavating trenches designed to receive a day's worth of waste. The soil from the excavation is often used for cover material and wind breaks. The ramp method is typically employed on sloping land, where waste is spread and compacted in a manner similar to the area method; however, the cover material is generally obtained from the front of the working face of the filling operation.

Modern landfill design often incorporates liners constructed of soil (e.g., recompacted clay) or synthetics (e.g., high density polyethylene), or both to provide an impermeable barrier to leachate (i.e., water that has passed through the landfill), and gas migration from the landfill.

### 7.8.2 Emission Control Measures

Landfill gas collection systems are either active or passive systems. Active collection systems provide a pressure gradient in order to extract landfill gas by use of mechanical blowers or compressors. Passive systems allow the natural pressure gradient created by the increased pressure within the landfill from landfill gas generation to mobilize the gas for collection.

Landfill gas control and treatment options include (1) combustion of the landfill gas and (2) purification of the landfill gas. Combustion techniques include techniques that do not recover energy (e.g., flares and thermal incinerators), and techniques that recover energy (i.e., gas turbines and internal combustion engines) and generate electricity from the combustion of landfill gas. Boilers can also be used to recover energy from landfill gas in the form of steam. These combustion techniques are not expected to provide any control of mercury emissions.

Purification techniques can be used to process raw landfill gas to pipeline quality natural gas by using adsorption, absorption, and membranes. Mercury emissions may be reduced by adsorption, but no data are available to determine the extent of control of mercury emissions (if any).

### 7.8.3 Emissions

Landfill gas, composed of approximately 50 percent methane and 50 percent CO<sub>2</sub>, is produced by anaerobic decomposition of MSW in landfills.<sup>121</sup> In 1994, MSW landfills were estimated to release 10.2 million Mg (11.2 million tons) of methane.<sup>121</sup> Landfill gas also contains trace constituents, including mercury. Mercury comes from the breakage of waste materials that contain mercury, such as certain types of batteries, fluorescent light bulbs, and light switches. Data from nine landfills show landfill gas mercury concentrations that range from  $7.0 \times 10^{-7}$  ppm to  $8.8 \times 10^{-4}$  ppm and average  $1.4 \times 10^{-4}$  ppm.<sup>123</sup> Data provided by EPA's Emission Factor and Inventory Group (EFIG) for the Freshkills Landfill in New York indicate landfill gas mercury concentrations between  $2.5 \times 10^{-3}$  ppm and  $7.1 \times 10^{-4}$  ppm.<sup>124</sup> The midpoint of the data from Freshkills,  $1.6 \times 10^{-3}$  ppm, was averaged with the other nine data points to calculate an average landfill gas mercury concentration of  $2.9 \times 10^{-4}$  ppm. Future releases of the EPA document "Compilation of Air Pollutant Emission Factors" (AP-42) will incorporate additional data (that is not yet available) for mercury emissions from MSW landfills in Section 2.4, Landfills.

Total 1994 mercury emissions from this source category are estimated to be 0.074 Mg (0.081 tons); see Appendix A for details.

## 7.9 GEOTHERMAL POWER PLANTS

Geothermal power plants are either dry-steam or water-dominated.<sup>125</sup> For dry-steam plants, steam is pumped from geothermal reservoirs to turbines at a temperature of about 180°C (360°F) and a pressure of 7.9 bars absolute. For water-dominated plants, water exists in the producing strata at a temperature of approximately 270°C (520°F) and at a pressure slightly higher than hydrostatic. As the water flows towards the surface, pressure decreases and steam is formed, which is used to operate the turbines. In 1992, 18 geothermal power plants were operating in the United States, and one new plant began operating in 1993.<sup>126,127</sup> Table 7-6 lists the names, locations, plant types, and capacities of these facilities.

TABLE 7-6. GEOTHERMAL POWER PLANTS OPERATING  
IN THE UNITED STATES IN 1992<sup>a</sup>

Facility	Type	Net capacity (MW)
The Geysers, CA	Dry-steam	1,805.7
Salton Sea, CA	Water-dominated	218.3
Heber, CA	Water-dominated	47.0
East Mesa, CA	Water-dominated	106.0
Coso, CA	Water-dominated	247.5
Casa Diablo, CA	Water-dominated	34.0
Amedee, CA	Water-dominated	2.0
Wendel, CA	Water-dominated	0.7
Puna, HI	Not specified	25.0
Dixie Valley, NV	Water-dominated	57.0
Steamboat Hot Springs, NV	Water-dominated	19.3
Beowawe Hot Springs, NV	Water-dominated	16.7
Desert Peak, NV	Water-dominated	9.0
Wabuska Hot Springs, NV	Water-dominated	1.7
Soda Lake, NV	Water-dominated	15.7
Stillwater, NV	Water-dominated	12.5
Empire and San Emidio, NV	Water-dominated	3.2
Roosevelt Hot Springs, UT	Water-dominated	20.0
Cove Fort, UT	Water-dominated	12.1
Total		2,653

Source: References 126 and 127.

<sup>a</sup>Puna, Hawaii data from Reference 127. Puna facility began operating in 1993. All other data taken from Reference 126.

#### 7.9.1 Emission Control Measures

No information is available pertaining to air pollution control systems used in geothermal power plants.

#### 7.9.2 Emissions

Mercury emissions at geothermal power plants are documented to result from two sources: off-gas ejectors, and cooling towers. Table 7-7 contains the mercury emission factors for these two sources. These data are based on measurements taken in 1977.<sup>125</sup> No process data are given in the documentation containing the test results and the primary source of these data could not be obtained to verify the validity of the emission factors. If significant process modifications or changes in control strategies have been incorporated since 1977, the emission factors reported in Table 7-7 may no longer be valid.

Total 1993 mercury emissions from this source category are estimated to be 1.3 Mg (1.4 tons); see Appendix A for details.

TABLE 7-7. MERCURY EMISSION FACTORS FOR GEOTHERMAL POWER PLANTS

Source	Emission factor range, g/MWe/hr	Average emission factor	
		g/MWe/hr	lb/MWe/hr
Off-gas ejectors	0.00075 - 0.02	0.00725	0.00002
Cooling tower exhaust	0.026 - 0.072	0.05	0.0001

Source: Reference 125.

## 7.10 PULP AND PAPER PRODUCTION

In the pulp and paper industry, wood pulp is produced from raw wood via chemical or mechanical means or a combination of both. When chemical pulping methods are used to produce pulp, the chemicals used in the process are recycled for reuse in the process. Combustion sources located in the chemical recovery area of pulp and paper mills represent potential sources of mercury emissions. Power boilers located at pulp mills are another potential source of mercury emissions; mercury emissions from power boilers are discussed in Sections 6.1 and 6.2. A list of the 153 U. S. pulp mills currently in operation that have chemical recovery combustion sources is provided in Appendix E. A description of the pulping processes and chemical recovery combustion sources at these pulp mills and the estimated mercury emissions from the chemical recovery combustion sources are discussed below.

### 7.10.1 Process Description<sup>128,129,130</sup>

The wood pulping process may involve chemical or mechanical treatment of the wood or a combination of both. Four principal chemical wood pulping processes currently in use are (1) kraft, (2) soda, (3) sulfite, and (4) semichemical. (The semichemical process requires both chemical and mechanical treatment of the wood.) The kraft process is the dominant pulping process in the United States, accounting for approximately 80 percent of domestic pulp production. Currently, there are estimated to be 122 kraft, 2 soda, 15 sulfite, and 14 stand-alone semichemical pulp mills in the United States with chemical recovery combustion sources.<sup>131,132,133</sup>

In the kraft pulping process, wood chips are "cooked" under pressure in a digester in an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S), referred to as "cooking liquor," or "white liquor." Cooking the wood chips in white liquor results in the extraction of cellulose from the wood by dissolving the lignin that binds the cellulose fibers together. The contents of the digester are then discharged to a blow tank, where the softened chips are disintegrated into fibers or "pulp."

The pulp and spent cooking liquor are subsequently separated in a series of brown stock washers. Spent cooking liquor, referred to as "weak black liquor," from the brown stock washers is routed to the chemical recovery area. Weak black liquor is a dilute solution of lignins, organic materials, sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and white liquor. The purpose of the chemical recovery area is to recover the cooking liquor chemicals from the spent cooking liquor. After the brown stock washers, the washed pulp may be subjected to a bleaching sequence, before being pressed and dried to yield the finished product.

Some of the mercury that is present in the wood chips will also be present in the finished product, and the rest will be present in the spent cooking liquor. The levels of mercury in the product and in the liquor are expected to be very low because the levels of mercury in the wood chips are not expected to be higher than the background levels of mercury in the environment. However, no data are currently available to confirm this assumption. The amount of mercury that is present in the wood chips is expected to vary somewhat from mill to mill based on the origin of the wood that the mills process.

Emissions of PM (including metals such as mercury) are associated with combustion units located in the chemical recovery area. The chemical recovery area at a kraft pulp mill includes chemical recovery furnaces, smelt dissolving tanks (SDT's), and lime kilns. Figure 7-8 shows the relationship of the chemical recovery cycle to the pulping and product forming process areas. Figure 7-9 shows a process flow diagram of the chemical recovery area at kraft pulp mills and identifies the mercury emission points.

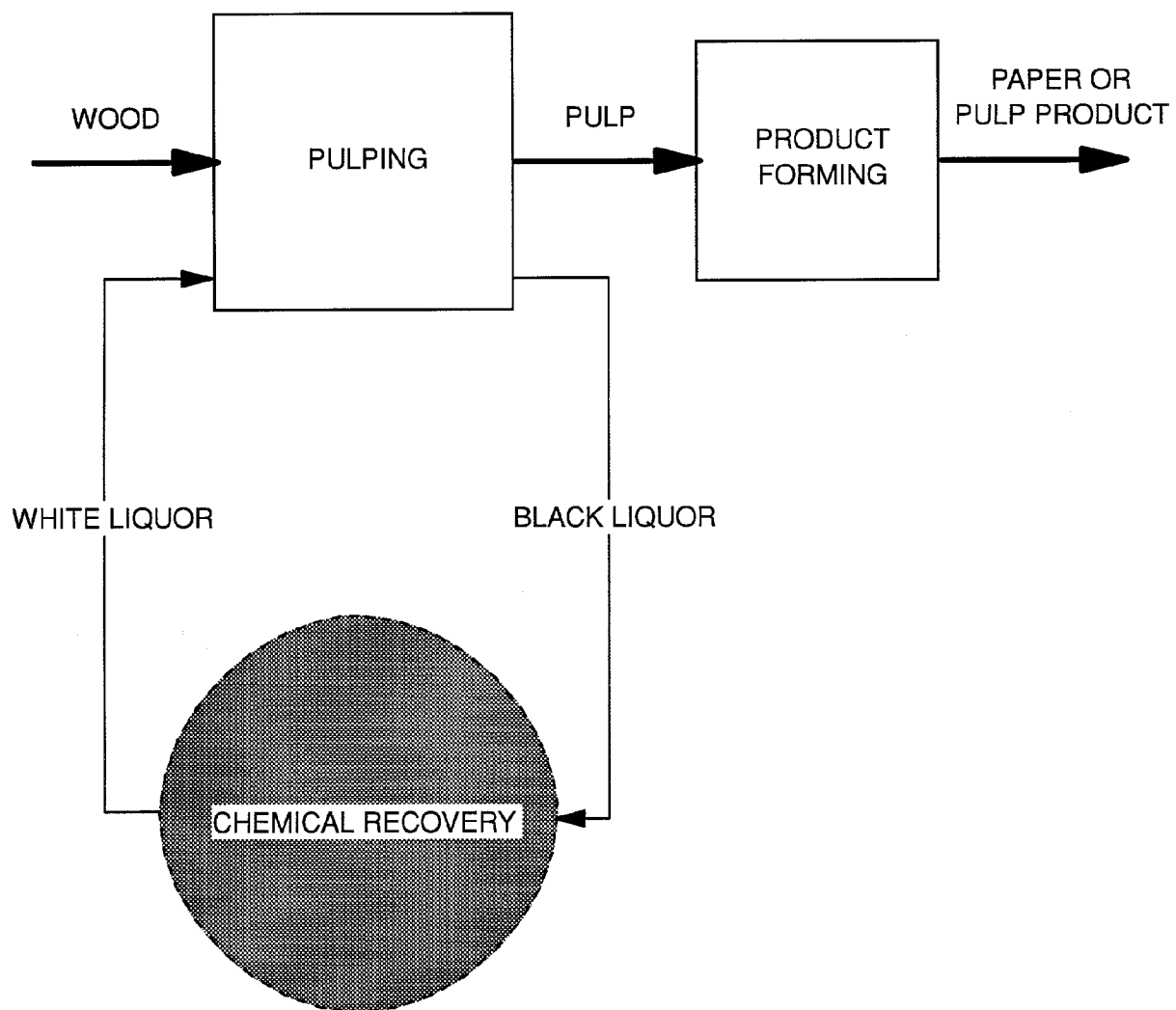


Figure 7-8. Relationship of the chemical recovery cycle to the pulping and product forming processes.<sup>128</sup>

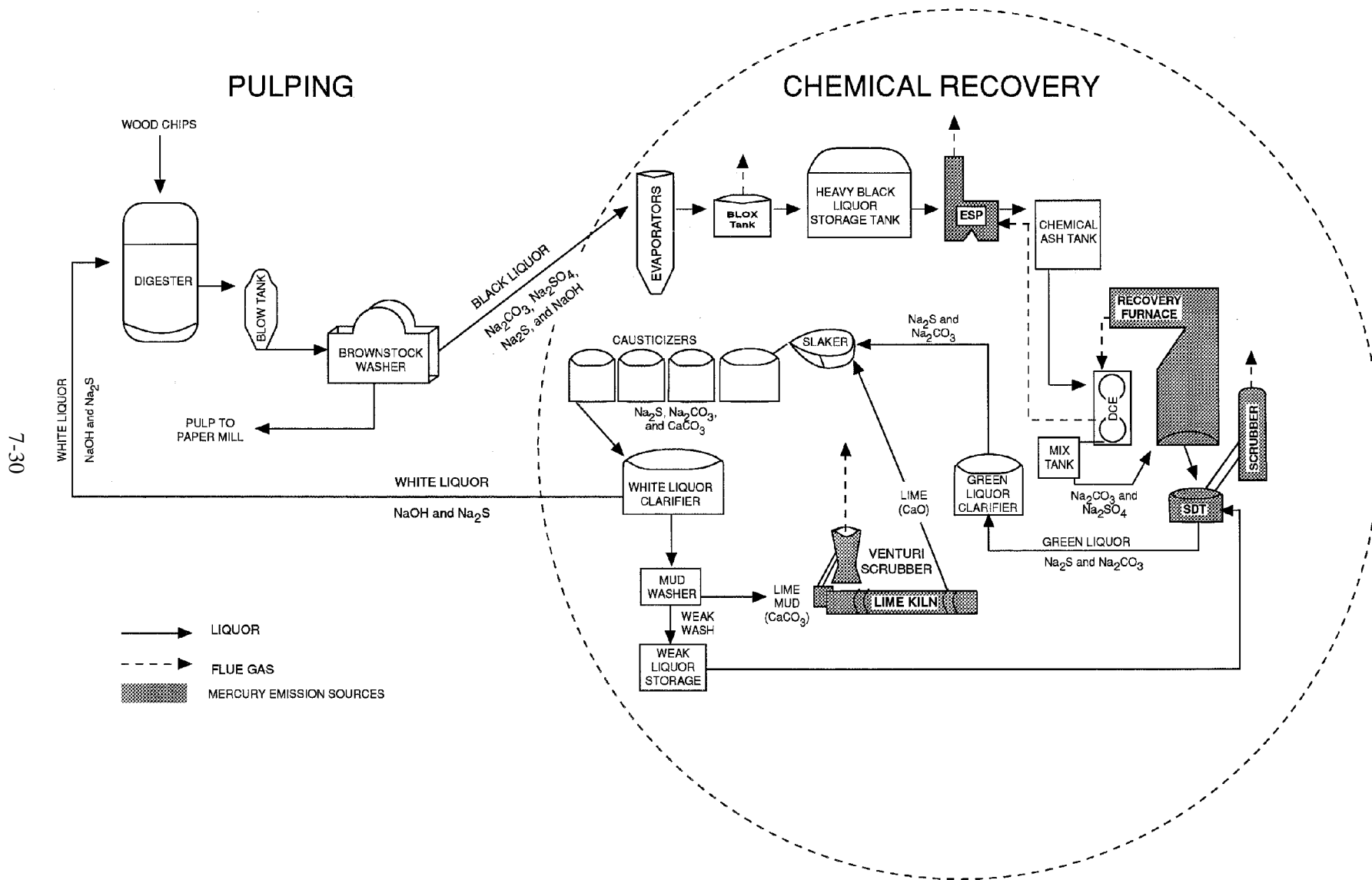


Figure 7-9. Kraft process--chemical recovery area (including direct contact evaporator recovery furnace).<sup>128</sup>



In the chemical recovery cycle, weak black liquor is first directed through a series of multiple-effect evaporators (MEE's) to increase the solids content of the black liquor. The "strong" black liquor from the MEE's is then either (1) oxidized in the black liquor oxidation (BLO) system if it is further concentrated in a direct contact evaporator (DCE) or (2) routed directly to a concentrator (i.e., nondirect contact evaporator [NDCE]).

Concentrated black liquor is then sprayed into the recovery furnace, where organic compounds are combusted, and the  $\text{Na}_2\text{SO}_4$  is reduced to  $\text{Na}_2\text{S}$ . The combustion process typically occurs at temperatures around  $982^\circ\text{C}$  ( $1800^\circ\text{F}$ ) or higher, which would be high enough to volatilize any mercury present in the black liquor. The black liquor burned in the recovery furnace has a high energy content, which is recovered as steam for process requirements at the pulp mill. The heat is recovered through the heat exchanger section of the furnace (i.e., superheater, boiler bank, and economizer). The design economizer exit gas temperature ranges from  $177$  to  $190^\circ\text{C}$  ( $350$  to  $375^\circ\text{F}$ ) for recovery furnaces with NDCE's (i.e., NDCE recovery furnaces). For recovery furnaces with DCE's (i.e., DCE recovery furnaces), the heat from the recovery furnace is used to evaporate the black liquor. As a result, the required economizer exit gas temperature for DCE recovery furnaces,  $371$  to  $427^\circ\text{C}$  ( $700$  to  $800^\circ\text{F}$ ), is much higher than that for NDCE recovery furnaces.

Based on the exit gas temperatures, there is no substantial difference in the potential for mercury to remain vaporized when it exits a DCE recovery furnace than an NDCE recovery furnace. However, most recovery furnaces are of the NDCE design. According to available data, approximately 61 percent of kraft and soda recovery furnaces are NDCE recovery furnaces, while 39 percent are DCE recovery furnaces. The NDCE recovery furnace design is a more recent design, with greater capacity, greater energy efficiency, and lower odorous total reduced sulfur (TRS) emissions. Most recovery furnaces installed since the 1970's have been NDCE recovery furnaces.

In addition to the steam energy provided by combustion of black liquor in the recovery furnace, energy for pulping processes at the mill can also be provided by a power boiler. Power boilers located at pulp and paper mills are usually wood-fired boilers, although coal-, oil-, gas-, and combination fuel-fired boilers are also used. Process and emissions information for these boilers are provided in Section 6.0.

After the black liquor has been combusted in the recovery furnace, molten inorganic salts, referred to as "smelt," collect in a char bed at the bottom of the furnace. Smelt, at approximately  $1040$  to  $1150^\circ\text{C}$  ( $1900$  to  $2100^\circ\text{F}$ ), is drawn off from the furnace and dissolved in weak wash water in the SDT to form a solution of carbonate salts called "green liquor," which is primarily  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$ . The green liquor formed in the SDT also contains insoluble unburned carbon and inorganic impurities, called dregs, which are removed in a series of clarification tanks.

Although the high temperature of the smelt discharged from the furnace is sufficient to volatilize any mercury present in the smelt, the smelt is cooled as it enters the SDT when it is shattered by high-pressure steam or shatter sprays of recirculated green liquor. Large volumes of steam are generated when the molten smelt is dissolved in the weak wash water, which releases more heat. The vapor space above the liquid level provides an opportunity for water vapor and PM resulting from the quenching of the smelt to settle out of suspension into the green liquor. An induced draft fan constantly draws the vapor and entrained PM through a PM control device, generally a wet scrubber. Because of the cooling of the smelt that occurs in the SDT, there is some opportunity for mercury to remain in the liquor upon exiting the SDT.

Decanted green liquor from the SDT is transferred to the causticizing area of the mill, where the  $\text{Na}_2\text{CO}_3$  is converted to  $\text{NaOH}$  by the addition of lime. The green liquor is first transferred to a slaker tank, where lime from the lime kiln reacts with water to form calcium hydroxide ( $\text{Ca}[\text{OH}]_2$ ). From the slaker, liquor flows through a series of agitated tanks, referred to as causticizers, that allow the causticizing reaction to go to completion (i.e.,  $\text{Ca}[\text{OH}]_2$  reacts with  $\text{Na}_2\text{CO}_3$  to form  $\text{NaOH}$  and  $\text{CaCO}_3$ ). The causticizing product is then routed to the white liquor clarifier, which removes  $\text{CaCO}_3$  precipitate, referred to as "lime mud." The lime mud, along with dregs from the green liquor clarifier, is washed in the mud washer to remove the last traces of sodium. The filtrate from the mud washer, known as "weak wash," is used in the SDT to dissolve recovery furnace smelt. The white liquor ( $\text{NaOH}$  and  $\text{Na}_2\text{S}$ ) from the clarifier is recycled to the digesters in the pulping area of the mill.

The mud from the mud washer is dried and calcined in the lime kiln to produce "reburned" lime, which is reintroduced to the slaker. The calcining reaction requires a minimum temperature of  $815^\circ\text{C}$  ( $1500^\circ\text{F}$ ), which is sufficient to volatilize any mercury present in the lime mud. The combustion gases exit

the lime mud feed end of the kiln at temperatures of approximately 150° to 200°C (300° to 400°F), which will also result in volatilization of mercury.

The other pulping processes are similar to the kraft pulping processes but with some significant differences. The soda pulping process is essentially the same as the kraft process, except that soda pulping is a nonsulfur process ( $\text{Na}_2\text{CO}_3$  only or a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ ), and, therefore, does not require black liquor oxidation to reduce the odorous TRS emissions.

The sulfite pulping process is also carried out in a manner similar to the kraft process, except that an acid cooking liquor is used to cook the wood chips. The sulfite chemical pulping processes currently used at U.S. mills can be classified as either acid sulfite or bisulfite; these processes use magnesium, ammonia, or calcium bases to buffer the sulfite cooking liquor. Chemical recovery is only practiced at those sulfite mills that use the magnesium or ammonia-based sulfite process. The system used to recover cooking chemicals is specific to the base. Similar to kraft pulp mills, the spent liquor is recovered at sulfite pulp mills by being burned in a type of combustion unit. Combustion units used at sulfite pulp mills include recovery furnaces and fluidized-bed reactors. Typical combustion temperatures for sulfite combustion units are about 278°C (500°F) lower relative to kraft recovery furnaces, ranging from 704° to 760°C (1300° to 1400°F). These temperatures are sufficiently high to volatilize any mercury present.

The semichemical pulping process is used to produce corrugating medium, which is the inside layer of corrugated containers. The semichemical pulping process uses a combination of chemical and mechanical pulping methods. Wood chips first are partially softened in a digester with chemicals, steam, and heat; once chips are softened, mechanical methods complete the pulping process. Three types of chemical pulping methods are currently in use at semichemical mills--neutral sulfite semichemical (NSSC) (sodium-based sulfite process), kraft green liquor, and nonsulfur ( $\text{Na}_2\text{CO}_3$  only or a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ ).

Semichemical and kraft pulping processes are co-located at 13 mills. At those mills, the spent liquor from the semichemical pulping process is burned in the kraft recovery furnace. Fourteen mills use the semichemical pulping process only. Those mills, referred to as "stand-alone semichemical pulp mills," use a variety of chemical recovery equipment for combusting the spent liquor, but the predominant type (50 percent) appears to be the fluidized-bed reactor. Other types of chemical recovery equipment used at stand-alone semichemical pulp mills include recovery furnaces, smelters, rotary liquor kilns, and pyrolysis units. Typical combustion temperatures in the recovery furnaces and smelters are similar to those for kraft and soda, while typical combustion temperatures in the fluidized-bed reactors and rotary liquor kilns are about 278°C (500°F) lower, around 704° to 760°C (1300° to 1400°F). These temperatures are sufficiently high to volatilize any mercury present.

Similar to the kraft process, cooking liquor chemicals at semichemical mills are recovered from the chemical recovery combustion equipment as ash or smelt, which is mixed with water in a dissolving tank to form green liquor. The green liquor is then combined with makeup chemicals to form fresh cooking liquor. A typical temperature at the dissolving tank vent would be 180°F, which is well below the volatilization temperature for mercury. Therefore, mercury is expected to be in particulate form at the dissolving tank vent.

#### 7.10.2 Emission Control Measures<sup>128,129,134</sup>

Due to State and Federal regulations regarding PM emissions, almost all chemical recovery combustion units at kraft pulp mills (i.e., recovery furnaces, SDT's, and lime kilns) are equipped with add-on PM control devices.

The PM emitted from kraft recovery furnaces is mainly  $\text{Na}_2\text{SO}_4$  (about 80 percent), with smaller amounts of  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaCl}$ . There are economic benefits from recycling the predominantly  $\text{Na}_2\text{SO}_4$  PM catch from the recovery furnace flue gases because the recovery of chemicals reduces the costs of using "makeup" chemicals. The PM emissions from approximately 95 percent of kraft recovery furnaces are controlled with an ESP alone; the PM emissions from the remaining furnaces are controlled with an ESP followed by a wet scrubber (4 percent) or with a wet scrubber alone (1 percent). Properly designed and operated ESP's used on kraft recovery furnaces routinely achieve PM removal efficiencies of 99 percent or greater. Direct-contact evaporators used to concentrate black liquor also serve to control PM emissions, removing between 20 and 50 percent of the particulate load prior to the ESP.

To obtain optimal control of PM on a continuous basis, the ESP should be operated at temperatures between 150° and 260°C (300° and 500°F). Below 150°C (300°F), corrosion is accelerated due to

concentration of acid gases; above 260°C (500°F), the ESP's PM collection efficiency starts to decline. Typical exit gas temperatures for ESP's installed on NDCE and DCE recovery furnaces would be 199 and 160°C (390 and 320°F), respectively. Recovery furnaces controlled with wet scrubbers would have even lower exit gas temperatures (e.g., 82°C [180°F]).

Finely divided smelt ( $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$ ) entrained in water vapor accounts for most of the PM emissions from SDT's. The PM emissions from approximately 87 percent of kraft SDT's are controlled with a wet scrubber. Venturi scrubbers are the most commonly used type of wet scrubber installed on SDT's, comprising about 43 percent of SDT wet scrubbers. Reported PM removal efficiencies for venturi scrubbers installed on SDT's range from 97 to greater than 99 percent. Typical inlet and outlet temperatures for SDT wet scrubbers would be 93 and 77°C (200 and 170°F), respectively. These temperatures are below the volatilization temperature for mercury. Therefore, it is expected that most of the mercury present will be in particulate form and should be collected by the wet scrubber.

Particulate matter emissions from most of the remaining SDT's (11 percent) are controlled with a mist eliminator alone. Mist eliminators are generally less effective than wet scrubbers at controlling PM emissions. Inlet and outlet temperatures for SDT mist eliminators are similar to those for SDT wet scrubbers, so any difference in mercury control relative to wet scrubbers would be a result of the lower PM control efficiency of mist eliminators relative to wet scrubbers.

Lime kiln PM emissions are mainly sodium salts,  $\text{CaCO}_3$ , and  $\text{CaO}$ , with uncontrolled emissions comprising mainly calcium compounds and controlled emissions comprising mainly sodium salts. Sodium salts result from the residual  $\text{Na}_2\text{S}$  in the lime mud after washing. There are economic advantages to recovering the PM emissions from lime kilns because after the PM is recovered, it can be returned to the system for calcining. Particulate matter emissions from approximately 90 percent of kraft lime kilns are controlled with a wet scrubber. Two percent of these scrubbers are operated in series with a second scrubber. Venturi scrubbers are the most commonly used type of wet scrubber installed on lime kilns, comprising about 89 percent of lime kiln wet scrubbers. Particulate matter collection efficiencies for venturi scrubbers installed on kraft lime kilns average 99 percent. Typical inlet and outlet temperatures for lime kiln venturi scrubbers would be 249 and 71°C (480 and 160°F), respectively. These temperatures are below the volatilization temperature for mercury. Therefore, it is expected that most of the mercury present will be in particulate form and should be collected by the venturi scrubber.

Particulate matter emissions from the remaining 10 percent of kraft lime kilns are controlled by ESP's (9 percent) or the combination of an ESP and wet scrubber (1 percent). Installing ESP's to control PM emissions from lime kilns has been more widespread in recent years; about half of the APCD installations on lime kilns since 1990 have been ESP's. Properly designed and operated ESP's used on kraft lime kilns routinely achieve PM removal efficiencies of 99 percent or greater. Typical inlet and outlet temperatures for the lime kiln ESP are expected to be similar, about 249°C (480°F). Although the outlet temperature for the ESP is higher than that for the lime kiln venturi scrubber, it is still below the volatilization temperature for mercury. Therefore, it is expected that most of the mercury will be in particulate form and should be collected by the ESP.

Some of the equipment operated downstream of the chemical recovery combustion units at sulfite pulp mills serve a dual role as process equipment and emission control equipment (e.g., absorption towers used to recover  $\text{SO}_2$  for reuse in the process and to reduce emissions to the atmosphere). Other equipment have been installed primarily to reduce emissions. Control devices installed to reduce PM emissions at sulfite pulp mills include fiber-bed mist eliminators and wet scrubbers. A typical exit gas temperature for these devices would be 49°C (120°F), which is below the volatilization temperature for mercury. Therefore, most of the mercury present should be in particulate form and should be recovered using the PM control devices.

Similar to sulfite pulp mills, some of the equipment installed downstream of the chemical recovery combustion unit at stand-alone semichemical pulp mills are used as both process equipment and emission control equipment. For example, in addition to controlling PM emissions, venturi scrubbers at some mills also serve as direct contact evaporators to increase the solids content of the black liquor. Other control devices installed to reduce PM emissions include cyclones and wet and dry ESP's. Typical exit gas temperatures for venturi scrubbers and ESP's installed on combustion units at semichemical pulp mills would be similar to those for comparable control devices installed on combustion units at kraft pulp mills.

Fugitive emissions from sources in a pulp mill include coal piles, paved and unpaved roads, bulk materials handling (lime, limestone, starch, etc.), and wood handling. Control strategies include wetting; the

use of chemical agents, building enclosures, and windscreens; paving or wetting roads; and modifying handling equipment. No information is available on the amount of mercury emitted as fugitive emissions, but the amount is expected to be very small, around background levels.

There are only limited emission test data from pulp and paper combustion sources on the performance of add-on controls for metals such as mercury. However, data collected from other combustion sources on the relative performance of add-on control devices for metals indicate that systems that achieve the greatest PM removal also provide the best performance for metals. Therefore, particulate mercury may also be controlled to the same extent as PM. Although no data are available for confirmation, some of the mercury may be emitted from the control devices in vapor form, especially from the ESP's, which have higher outlet temperatures compared to the wet scrubbers.

### 7.10.3 Emissions

Mercury can be introduced into the pulping process through the wood which is being pulped, in the process water used in the pulping process, and as a contaminant in makeup chemicals added to the process. If the mercury is not purged from the process in the wastewater or as dregs, it can accumulate in the chemical recovery area and subsequently be emitted from the chemical recovery combustion sources. The amount of mercury emitted may depend on how tightly closed the pulping process is (i.e., the degree to which process waters are recycled and reused). Mercury emission points in the chemical recovery area are shown in Figure 7-9.

Mercury emissions data are only available from combustion units at kraft pulp mills. Detectable mercury emissions data are available for eight recovery furnaces, one SDT, and three lime kilns, located at 11 kraft pulp mills. The mercury emissions data for these kraft combustion units were summarized in a memorandum based on the following sources: (1) test data presented in Technical Bulletin No. 650 from the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI), (2) test data provided in a response to a survey sent to pulp and paper mills, and (3) test data in emission test reports provided by pulp and paper mills.<sup>135</sup>

Average mercury emission factors were estimated for recovery furnaces, SDT's, and lime kilns based on the available mercury emissions data. The average mercury emission factors for the recovery furnaces, SDT, and lime kilns are presented in Table 7-8. Where necessary, test data were blank corrected to be consistent with EPA Method 29 procedures (which can be used to measure mercury emissions).<sup>136</sup> Only those emission tests that had detectable emissions in at least one test run were included in the mercury average. For those test runs with nondetect data, the values of the nondetects were calculated as one-half the detection limit. Data sets for which all three runs were below method detection limits were not included in the average.

Nationwide 1994 mercury emissions were estimated from these emission factors for kraft and soda recovery furnaces, SDT's, and lime kilns. The total mercury emissions were estimated to be 1.6 Mg (1.8 tons); see Appendix A for details. As shown in Appendix A, the single largest source of mercury emissions in the chemical recovery area is the recovery furnace. Nationwide, mercury emissions account for only 0.003 percent of PM emissions from kraft and soda recovery furnaces, SDT's, and lime kilns.<sup>137</sup>

TABLE 7-8. MERCURY EMISSION FACTORS FOR COMBUSTION SOURCES AT PULP AND PAPER MILLS

Kraft combustion source	Emission factor		Number of units tested/control device
	kg/Mg	lb/ton	
Recovery furnace	$1.95 \times 10^{-5} \text{ }^a$	$3.90 \times 10^{-5} \text{ }^a$	Eight recovery furnaces, each controlled with an ESP
Smelt dissolving tank	$2.61 \times 10^{-8} \text{ }^a$	$5.23 \times 10^{-8} \text{ }^a$	One SDT, controlled with a mist eliminator
Lime kiln	$1.46 \times 10^{-6} \text{ }^b$	$2.91 \times 10^{-6} \text{ }^b$	Three lime kilns, each controlled with a wet scrubber

Source: Reference 135.

<sup>a</sup>Per Mg (or ton) of black liquor solids fired in the recovery furnace.

<sup>b</sup>Per Mg (or ton) of lime produced in the lime kiln.

## 8.0 EMISSIONS FROM MISCELLANEOUS FUGITIVE AND AREA SOURCES

Mercury has been found to be emitted from various miscellaneous fugitive and area sources including the following:

1. Mercury catalysts;
2. Dental alloys;
3. Mobile sources;
4. Crematories;
5. Paint use;
6. Soil dust; and
7. Natural sources

Nationwide mercury emission estimates were developed only for the dental alloy and crematories source categories. For the remaining categories, either mercury use has been discontinued or no emission factors could be identified. Mercury emissions from dental alloys were estimated to be 0.64 Mg (0.7 tons) and emissions from crematories were estimated to be 0.73 Mg (0.80 tons).

### 8.1 MERCURY CATALYSTS

Mercury catalysts have been used in the production of polyurethane and vinyl chloride. According to 1995 data, U.S. consumption of refined mercury for "other chemical and allied products" includes pharmaceuticals and miscellaneous catalysts. This category is no longer reported as a separate category but is included in the "other uses" category. No data are available for any quantities of mercury used for catalytic purposes.<sup>2</sup>

#### 8.1.1 Process Description

Catalysts involved in the production of polyurethane have been composed of the phenylmercuric compounds ( $C_6H_5Hg^+$ ), but few facilities currently use this catalyst and phenylmercuric compounds are no longer produced in the United States.<sup>11</sup> The locations of facilities using these compounds are unknown.

Two processes can be used to manufacture vinyl chloride: one process based on acetylene uses mercuric chloride on carbon pellets as a catalyst, and the other is based on the oxychlorination of ethylene. Vinyl chloride is produced by oxychlorination at all facilities except at Borden Chemical and Plastics Corporation in Geismar, Louisiana. Borden Chemical and Plastics produces vinyl chloride using mercuric chloride as a catalyst with acetylene.<sup>11</sup>

#### 8.1.2 Emission Control Measures

No information was found in the literature concerning specific control measures for mercury emissions from the production of vinyl chloride.

#### 8.1.3 Emissions

No emission factors were found in the literature, and no test data that could be used to calculate emission factors was found. In the 1994 TRI inventory, Borden Chemical and Plastics reported no mercury emissions at the Louisiana production facility.<sup>3</sup>

## 8.2 DENTAL ALLOYS

Dental amalgams used to fill cavities in teeth include an appreciable quantity of mercury. The amalgamation process is fairly generic industrywide, although some dental facilities use ready-made dental capsules to reduce worker exposure to elemental mercury. Dental fillings contain mixtures of metals, usually silver (67 to 70 percent), tin (25 to 28 percent), copper (0 to 5 percent), and zinc (0 to 2 percent), which are blended with mercury in a 5:8 proportion to form an amalgam.<sup>8</sup>

### 8.2.1 Process Description

The dental alloy and mercury are placed inside a two-part plastic capsule that contains a pestle. Mercury is added with a dispenser that delivers a drop (or "spill") when a button is pressed. Usually, only one or two drops are necessary to mix the amalgam. The plastic capsule then is closed and placed in an agitator where the contents are mixed for approximately 15 seconds. Once mixing is completed, the capsule is opened to remove the amalgam, which then is placed in a container for immediate application in the cavity.<sup>8</sup>

### 8.2.2 Emission Control Measures

No emission controls are noted for handling mercury used in amalgam production. One work practice is the use of ready-made dental capsules that already contain a pestle and premeasured amounts of mercury and alloy.<sup>8</sup> This practice eliminates any unnecessary handling and accidental spilling of mercury.

### 8.2.3 Emissions

The total amount of mercury used in the dental industry in 1995 was 32 Mg (35 tons); this accounts for about 7 percent of the industrial consumption of mercury.<sup>2</sup> A 1981 report estimates that 2 percent of the mercury used in dental applications is emitted to the atmosphere.<sup>138</sup> Using the 2 percent figure, 1995 mercury emissions are estimated to be 0.64 Mg (0.7 tons); see Appendix A for estimation procedure.

## 8.3 MOBILE SOURCES

For the purposes of this document, mobile sources are defined as diesel- and gasoline-powered, on-road vehicles. The potential for emissions from other types of mobile sources such as ships, motorcycles, snowmobiles, and other nonhighway mobile sources are not included in this section due to absence of data.

A 1983 study indicated an estimated mercury emission factor of  $1.3 \times 10^{-3}$  milligram (mg) per kilometer (km) ( $4.6 \times 10^{-9}$  lb/mile) for motor vehicles without resolution of emission rates into vehicle types.<sup>139</sup> The population of vehicles studied was 81.9 percent gasoline-powered passenger cars, 2.4 percent gasoline-powered trucks, and 15.7 percent diesel trucks. This emission factor was based on a 1977 ambient sampling study, which was before the widespread use of catalytic converters and unleaded gasoline, and before State-regulated inspection and maintenance programs were widely mandated. Additionally, both gasoline and diesel vehicles are now subject to much more stringent tailpipe emission standards than they were in 1977. Thus, any emissions of mercury from highway motor vehicles are likely to be substantially reduced from 1977 levels. A 1979 study characterized regulated and unregulated exhaust emissions from catalyst and non-catalyst equipped light-duty gasoline operated automobiles operating under malfunction conditions.<sup>140</sup> An analysis for mercury was included in the study but no mercury was detected; the analytical minimum detection limit was not stated. A 1989 study measured the exhaust emission rates of selected toxic substances for two late model gasoline-powered passenger cars.<sup>141</sup> The two vehicles were operated over the Federal Test Procedure (FTP), the Highway Fuel Economy Test (HFET), and the New York City Cycle (NYCC). Mercury was among the group of metals analyzed but was not present in detectable quantities. The analytical minimum detection limits for mercury in the three test procedures were: FTP--0.025 mg/km ( $8.9 \times 10^{-8}$  lb/mile) HFET--0.019 mg/km ( $6.7 \times 10^{-8}$  lb/mi), and NYCC--0.15 mg/km ( $53.2 \times 10^{-8}$  lb/mi).<sup>142</sup> These minimum detection limits are over ten times higher than the estimated emission factor presented in the 1983 study. Because of the large differences between the mercury emission factors and the overall lack of test data, no average mercury emission factor is recommended for this source.

## 8.4 CREMATORIES

Mercury resulting from the thermal instability of mercury alloys of amalgam tooth fillings during cremation of human bodies may potentially be a source of mercury air emissions. In 1995, approximately 488,224 cremations were performed at the 1,155 crematories located throughout the United States.<sup>143</sup> Table 8-1 lists the number of crematories located in each State and the estimated number of cremations performed in each State for 1995 and projections of these totals for the years 1996, 2000, and 2010.

Only one set of data are available for the average quantity of mercury emitted for a cremation in the United States. Tests were conducted for a propane-fired incinerator at a crematorium in California. Results of the testing for uncontrolled mercury emissions ranged from 6.26 E-03 to 2.26 E-03 kg/body burned (1.38 E-04 to 4.9 E-03 lb/body); the average mercury emission factor was 1.50 E-03 kg/body burned (3.3 E-03 lb/body). The test results were obtained from tests conducted by the California Air Resources Board.<sup>144</sup>

Total 1995 mercury emissions from this category are estimated to be 0.73 Mg (0.80 tons); see Appendix A for details.

## 8.5 PAINT USE

Four mercury compounds--phenylmercuric acetate, 3-(chloromethoxy) propylmercuric acetate, di(phenylmercury) dodeceny succinate, and phenylmercuric oleate--were registered as biocides for interior and exterior paint but in May 1991, all registrations for mercury-based biocides in paints were voluntarily cancelled by the registrants.<sup>33</sup> According to the 1996 EPA Report to Congress, the demand for mercury to be used in paints was eliminated in 1992.

Mercury compounds were added to paints to preserve the paint in the can by controlling microbial growth and to preserve the paint film from mildew attack after it is applied to a surface. During and after application of paint, these mercury compounds can be emitted into the atmosphere. One source estimates that 66 percent of the mercury used in paints is emitted into the atmosphere; however, this emission rate, which was derived using engineering judgement, is based on a 1975 study performed when the demand for mercury in paint was high.<sup>145</sup> The age of the data and the method by which the emission factor was calculated limit the reliability of the factor, making emission estimates generated from it quite uncertain. Furthermore, no conclusive information is available regarding the time frame over which mercury in paint is emitted into the atmosphere after it is applied to a surface. However, limited information suggests that emissions could occur for as long as 7 years after initial application, although the distribution of emissions over this time period is unknown.<sup>38</sup> Based on the voluntary cancellation of mercury-based biocide registrations in May 1991 and rapidly declining usage in 1990, it is assumed that current mercury emissions from this source are very small or zero.

## 8.6 SOIL DUST

**[This section is the same as it appeared in the 1993 document.]**

Mercury levels in soil dust have been measured at a few locations in the western United States.<sup>146</sup> The mercury level in soil dust near a phosphate fertilizer operation in Pocatello, Idaho was found to be 0.002 (20 ppm) weight percent and levels in dust from an unpaved road near the same facility were at 0.001 weight percent. This reference also cited mercury levels to be about 0.001 weight percent in soil dust near a courthouse in Medford, Oregon; at a school in Bend, Oregon; near the downtown area of Grant's Pass, Oregon; and near Key Back in Eugene, Oregon. Samples taken near a silicone manufacturing plant in Springfield, Oregon, showed mercury levels at 0.004 weight percent in the soil dust. Tests at LaGrande dock in LaGrande, Oregon, showed mercury in the soil dust at levels of 0.003 weight percent.

The validity of these levels cannot be verified because the original references could not be located to evaluate the test methods and procedures used in these studies. In addition, the mercury levels found in the soils of these areas probably are not indicative of soil levels in other areas of the country. The soils in the Idaho and Oregon areas are primarily volcanic in geologic origin and have higher soil mercury levels than other areas of the U.S.



TABLE 8-1. NUMBER OF CREMATORIES AND CREMATIONS BY STATE

	1995 Crematories	1995 Cremations	Projected					
			1996 Crematories	1996 Cremations	2000 Crematories	2000 Cremations	2010 Crematories	2010 Cremations
<b>United States</b>	<b>1,155</b>	<b>488,224</b>	<b>1,177</b>	<b>514,100</b>	<b>1,321</b>	<b>606,200</b>	<b>1,678</b>	<b>836,500</b>
<b>New England</b>	<b>47</b>	<b>30,268</b>	<b>46</b>	<b>32,500</b>	<b>49</b>	<b>41,200</b>	<b>57</b>	<b>62,800</b>
Connecticut	11	6,336						
Maine	4	4,079						
Massachusetts	13	11,979						
New Hampshire	8	2,945						
Rhode Island	6	2,759						
Vermont	5	2,170						
<b>Middle Atlantic</b>	<b>110</b>	<b>64,570</b>	<b>109</b>	<b>66,900</b>	<b>117</b>	<b>78,400</b>	<b>138</b>	<b>107,300</b>
New Jersey	17	18,385						
New York	43	27,629						
Pennsylvania	50	18,556						
<b>East North Central</b>	<b>197</b>	<b>70,707</b>	<b>202</b>	<b>76,000</b>	<b>227</b>	<b>93,900</b>	<b>288</b>	<b>138,800</b>
Illinois	48	20,579						
Indiana	28	5,964						
Michigan	40	17,529						
Ohio	49	18,083						
Wisconsin	32	8,552						
<b>West North Central</b>	<b>83</b>	<b>21,229</b>	<b>86</b>	<b>24,600</b>	<b>97</b>	<b>29,800</b>	<b>123</b>	<b>42,800</b>
Iowa	16	3,448						
Kansas	9	1,918						
Minnesota	22	8,501						
Missouri	24	5,356						
Nebraska	7	2,006						
North Dakota	2	NA						
South Dakota	3	NA						

TABLE 8-1. (continued)

	1995 Crematories	1995 Cremations	Projected					
			1996 Crematories	1996 Cremations	2000 Crematories	2000 Cremations	2010 Crematories	2010 Cremations
<b>South Atlantic</b>	<b>247</b>	<b>95,894</b>	<b>247</b>	<b>100,500</b>	<b>294</b>	<b>119,200</b>	<b>413</b>	<b>165,900</b>
Delaware	4	1,245						
D.C.	0	NA						
Florida	124	61,070						
Georgia	21	6,086						
Maryland	17	6,797						
N. Carolina	31	8,074						
S. Carolina	14	3,127						
Virginia	29	8,396						
W. Virginia	7	1,099						
<b>East South Central</b>	<b>30</b>	<b>7,493</b>	<b>30</b>	<b>8,400</b>	<b>37</b>	<b>11,400</b>	<b>53</b>	<b>18,900</b>
Alabama	9	1,661						
Kentucky	5	1,768						
Mississippi	4	1,077						
Tennessee	12	2,987						
<b>West South Central</b>	<b>70</b>	<b>23,800</b>	<b>74</b>	<b>26,000</b>	<b>83</b>	<b>33,400</b>	<b>105</b>	<b>51,900</b>
Arkansas	12	3,039						
Louisiana	7	2,923						
Oklahoma	9	2,193						
Texas	42	15,645						
<b>Mountain</b>	<b>120</b>	<b>41,554</b>	<b>126</b>	<b>44,200</b>	<b>144</b>	<b>51,800</b>	<b>187</b>	<b>70,900</b>
Arizona	30	13,479						
Colorado	28	10,408						
Idaho	14	2,895						
Montana	15	3,402						
Nevada	12	6,557						
New Mexico	12	3,264						

TABLE 8-1. (continued)

	1995 Crematories	1995 Cremations	Projected					
			1996 Crematories	1996 Cremations	2000 Crematories	2000 Cremations	2010 Crematories	2010 Cremations
Utah	6	1,549						
Wyoming	3	NA						
<b>Pacific</b>	<b>251</b>	<b>131,405</b>	<b>257</b>	<b>135,000</b>	<b>273</b>	<b>147,100</b>	<b>314</b>	<b>177,200</b>
Alaska	6	1,328						
California	147	92,646						
Hawaii	8	4,214						
Oregon	37	11,736						
Washington	53	21,481						

Source: Reference 143.

## 8.7 NATURAL SOURCES OF MERCURY EMISSIONS

**[This section is the same as it appeared in the 1993 document.]**

Mercury is emitted from natural sources (rock, soils, water and biota) primarily as elemental mercury vapor and to a lesser degree as particulate and vaporous oxides, sulfides and halides of mercury. Organomercuric compounds (methylmercury vapors) are also a significant component of natural emissions (some evidence of dimethyl-mercury emissions also exists).<sup>147</sup> However, few direct measurements of mercury flux and speciation from natural sources are available in the literature. There is general agreement that the principal natural sources of mercury emissions include, in order of probable importance, volatilization in marine and other aquatic environments, volatilization from vegetation, degassing of geologic materials, PM and vapor emissions during volcanic and geothermal activity, wind-blown dust, and PM and vapor emissions during forest and brush fires. Recent studies strongly emphasize the importance of the air-water exchange of mercury as well as biologically mediated volatilization in both marine and terrestrial environments.<sup>147-150</sup> These sources represent a relatively constant flux to the atmosphere and may comprise 30 to 50 percent of total natural emissions.<sup>150</sup> In contrast, volcanic, geothermal, and burning biomass activities are widely variable temporally and spatially. Volcanic eruptions, in particular, can cause massive perturbations in atmospheric trace metal cycles. Volcanic activity alone may comprise 40 to 50 percent of total natural mercury emissions at times.<sup>150</sup>

Published estimates of total global emissions of mercury from natural sources range widely from 100 to 30,000 megagrams (Mg) (110 to 33,000 tons) per year. However, the more recent estimates cluster in the 2,000 to 3,000 Mg per year range.<sup>147</sup> Reference 147, citing work done in 1988, estimates natural emissions to be 3,000 Mg (3,300 tons) per year or approximately 40 percent of total global emissions from all sources. The supporting data for individual source categories are limited for each of these estimates, and it is clear that any quantitative understanding of natural mercury flux is lacking.

As a result of reemission, current levels of mercury emitted to the atmosphere by natural processes are elevated relative to preindustrial levels. More than two thirds of world mercury production has occurred since 1900, and mercury emissions have been widely dispersed and recycled. In other words, present day emissions from natural sources are comprised of yesterday's anthropogenic emissions, in part. It is not possible to quantify the contribution of recycled mercury to the natural emissions estimates and, therefore, the estimates cited above must be viewed with even greater uncertainty.